PRELIMINARY STUDY OF POSSIBLE REARRANGEMENT OF EPOXIDYL FREE RADICAL

A THESIS

SUBMITTED TO THE FACULTY OF CLARK ATLANTA UNIVERSITY IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE

BY

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ABSTRACT

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PRELIMINARY STUDY OF THE POSSIBLE REARRANGEMENT OF EPOXIDYL FREE RADICALS

Advisor: Dr. H. C. McBay

Thesis dated February, 1994

Evidence presented shows that bibenzyl was produced through pyrolysis and photolysis of styrene oxide. This supports McBay's[2] postulate that decomposition of styrene oxide results in the production of the alpha styrene epoxidyl free radical, which rearranges to form the phenacyl free radical. Further successive rearrangement and decarbonylation of this radical ultimately results in the formation of bibenzyl. However, photobromination of styrene oxide did not generate the phenacyl free radical requried to produce bibenzyl, rather, polymeric styrene was produced.

Also reported is the rearrangements of epoxidyl free radical generated through pyrolysis and photolysis of 2,3 epoxy butane. Pyrolysis at 450°C indicated that the resulting epoxidyl radical eventually forms 3,4 dimethyl 2,5 hexane-di-one. The reported results obtained from efforts on the aliphatic epoxidyl radical are thus far inconclusive. The technique for pyrolysis of these epoxides may well be optimized, and these investigations are ongoing. The photolysis of 2,3 epoxy butane under conditions which are effective for the aryl-substituted epoxides was ineffective with this aliphatic epoxide.

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ACKNOWLEDGMENTS

I dedicate this work to my Lord and Savior who made this project possible and to my mother, Mrs. Rose U. Ndu for her continuing loving support. I also acknowledge my appreciation to my husband and daughter Johnbull and Amara Nwagu for their love, patience and understanding during this time consuming endeavor. My many thanks to Chief I. O. Okwusogu and my brothers for their moral support.

I wish to express my deepest gratitude to my advisor, Dr. Henry McBay for his guidance encouragement and useful suggestions towards this work.

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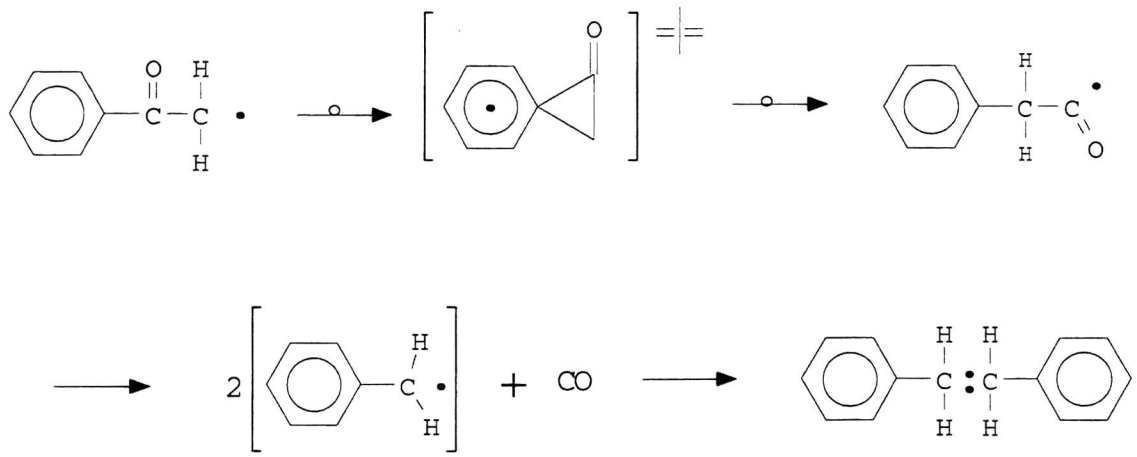
CHAPTER 1

HISTORICAL INTRODUCTION

1.1 SYNTHESIS OF BIBENZYL

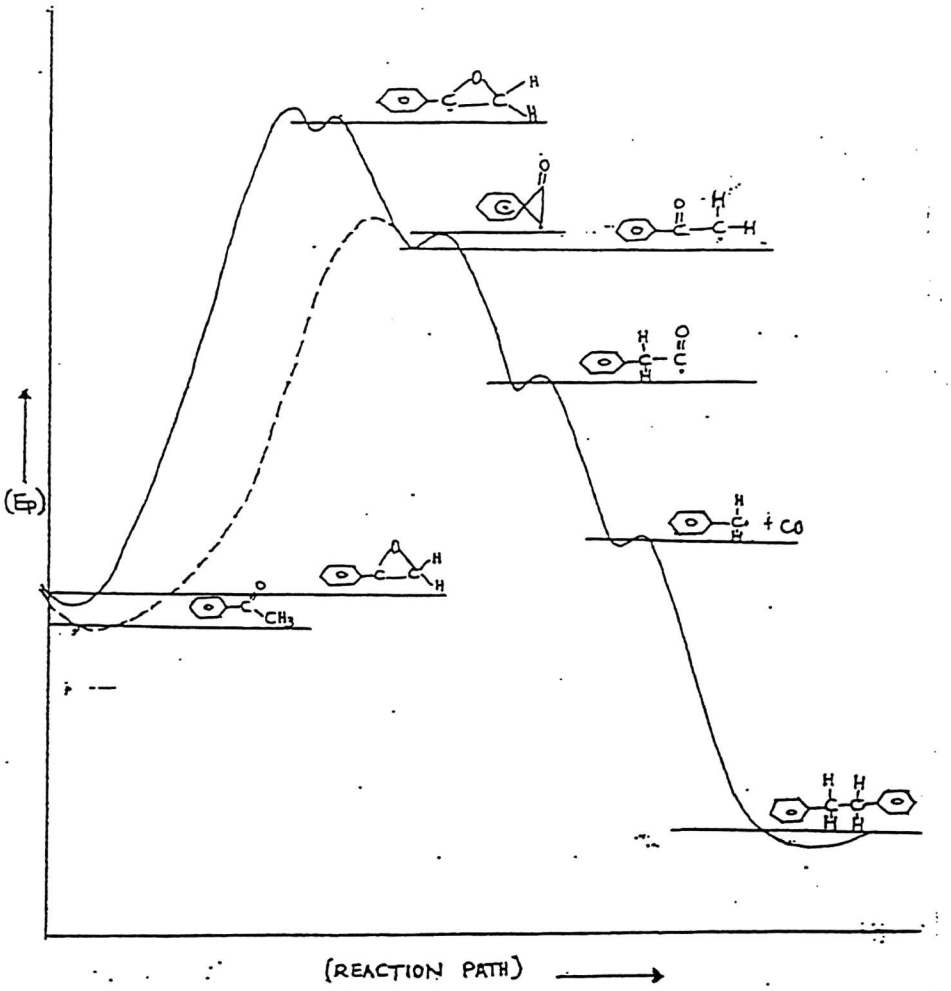
Reports[1] of earlier studies in this laboratory include evidence which depicts the kinetics and the mechanism of the neophyl-type rearrangement of the benzoyl methyl free radical. That evidence requires that the rearrangement be described as being intramolecular, with no fragmentation during the actual rearrangement.



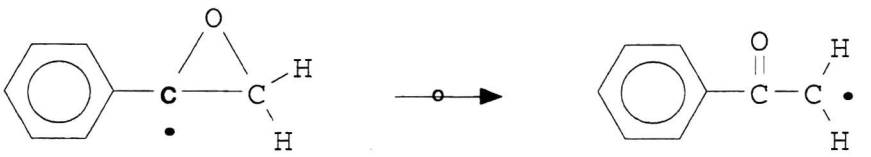
All efforts to obtain direct evidence for the occurrence of the 1-keto-spiro(2.5)-octadienyl-5'6' have failed, and it has therefore been described as a transition state[1b]. The schematic potential energy profile for this process and the kinetic data here implied are given as the following: See figure 1 page 2, references 2,3,4,and 10. Superimposed on this profile is the potential energy profile depicting the rearrangement of the analogous epoxidyl free radical here reported and its relationship to these earlier studies.

FIGURE 1

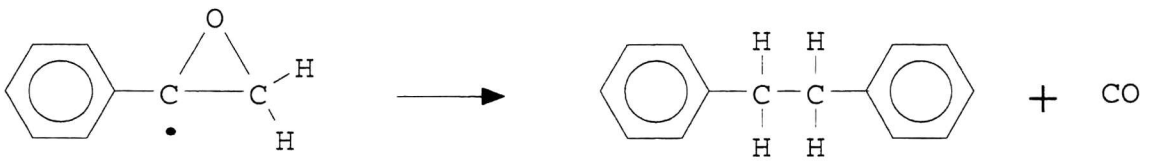
POTENTIAL ENERGY PROFILE FOR THE REARRANGEMENT OF EPOXIDYL FREE RADICAL GENERATED FROM STYRENE OXIDE



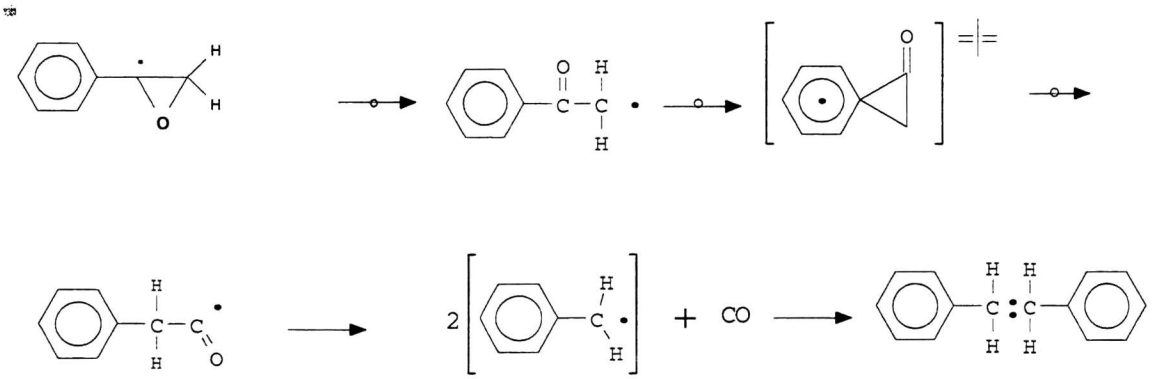
The evidence reported is the result of further interest to examine and possibly to understand the nature of this profile, particularly in the vicinity of this supposed transition state. This interest has led to the study of the rearrangement of epoxidyl free radicals, especially the alpha styrene epoxidyl free radical. Preliminary evidence reported supports the postulate that the alpha styrene epoxidyl free radical rearranges as follows:



Since the ultimate fate of the benzoyl methyl free radical at temperatures attending these studies is well-known[3,1b] to be bibenzyl, one takes as indirect evidence of the occurrence of this rearrangement the fact that bibenzyl is the ultimate product isolated and characterized.

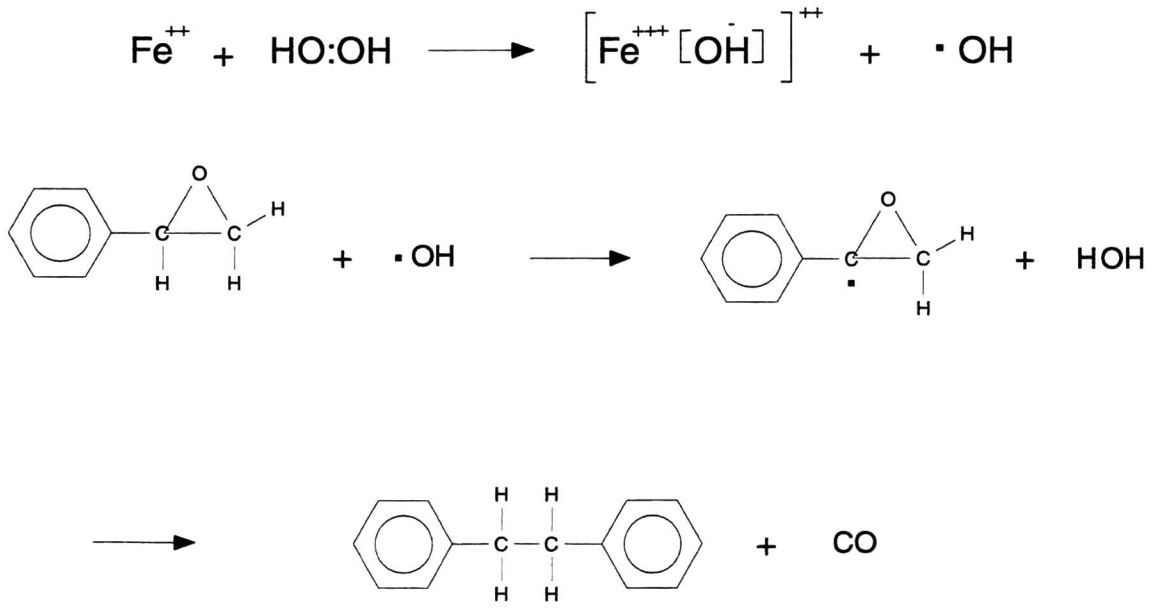


The suggested overall mechanism is the following:



It is significant to note that the earlier studies of Greene[1a] provide evidence which is consistent with the interpretation reported. Greene reported the irradiation of styrene oxide with ultra violet rays, gamma rays from $Co.^{60}$ and I^{127}. Although Greene was unable to resolve the resinous material obtained from his photolysis of styrene oxide, he did indeed collect a gas which he presumed to be "air" that was released from the reaction mixture during photolysis. He made careful determinations of the molecular weight of this gas by The Regnault method, and reported molecular weight values ranging from 26.6 to 28.81. It is now apparent that this gas was carbon monoxide whose molecular weight is 28.0 and this supports the postulate that carbon monoxide will be released in order to form benzyl radical.

Bluncson[10] did not report a molecular weight determination, but she obtained this gas, carbon monoxide, in her studies on the generation of alpha styrene epoxidyl free radical using the hydroxyl radical, generated by the Fenton reaction, as the hydrogen abstracting particle. This was done at -10°C.



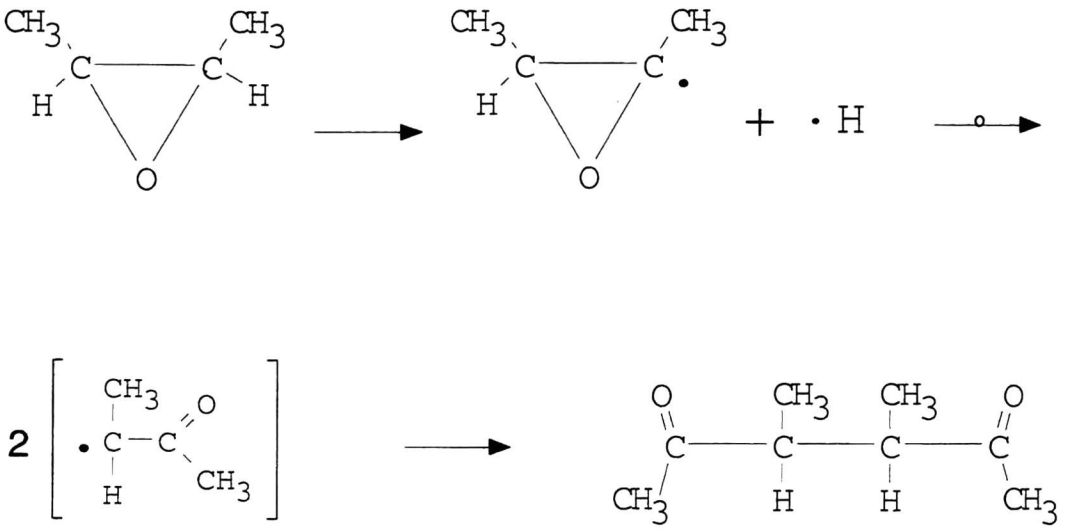
Bluncson[10] demonstrated that towards the end of this reaction, as the concentration of the Werner complex, (Fe^{+++} $(OH)^{-}$ $(OH_2)_5)^{++}$), increases, this species seems to absorb the carbon monoxide.

$$[Fe^{+++}\ OH\ [OH_2]_5]^{++} + 5CO \longrightarrow [Fe^{+++}\ \bar{O}H\ [CO]_5]^{++} + 5OH_2$$

At the onset of reaction, this gas is rapidly evolved, but during the later half of the reaction time, no gas was collected in the gas collecting chamber. Indeed when the residue in the reaction vessel was treated with ligands such as cyanide ion and pyridine, the remaining carbon monoxide gas slowly evolved. It is clear that both Greene and Bluncson accomplished this rearrangement of the epoxidyl radical, but neither was able to isolate and characterize the cognate product, bibenzyl, from their polymerized by-product. In the effort reported this latter objective has been accomplished.

1.2 ATTEMPTED SYNTHESIS OF 2,3 DIMETHYL 1,4 HEXA-DI-ONE

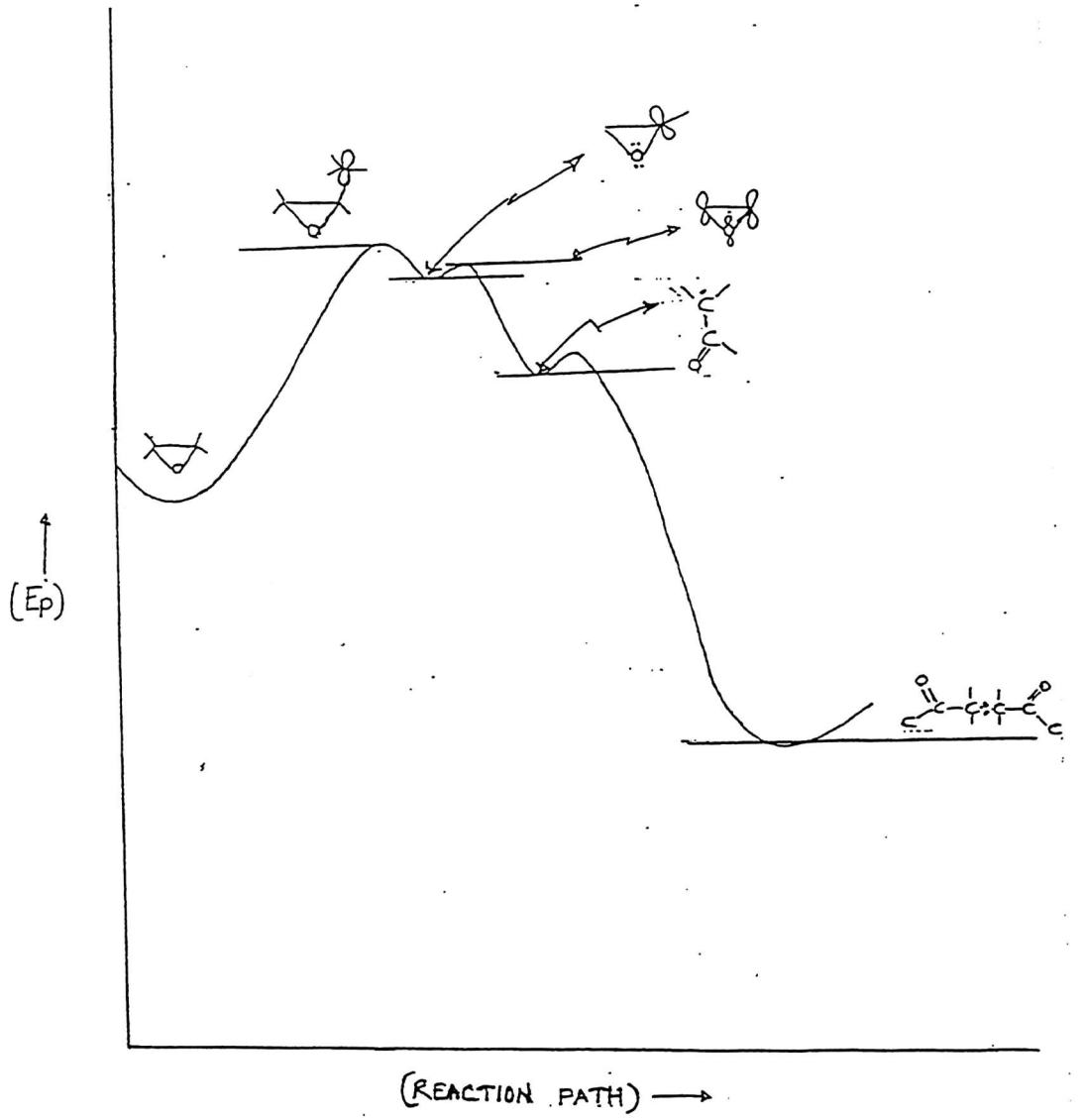
Extensive literature search on the synthesis of 3,4 dimethyl, 1,4 hexa-di-one revealed that nothing has been recorded on this subject using photolytic or thermal decomposition to generate the epoxidyl free radical intermediate radical or any such radical intermediate. Most of the works reported were on photolytic and thermal decomposition of butanone[4] and cylobutanone[5]. Evidence in these reports indicate a homogenous, unimolecular process and a diradical intermediate. All reports found in the literature had no direct bearing to this reaction. The suggested method to generate 3,4 dimethyl 1,4 hexa-di-one via an epoxidyl free radical is given by this overall scheme outlined below:



The suggested schematic potential energy profile for this process is given below:

FIGURE 2

POTENTIAL ENERGY PROFILE FOR THE ATTEMPTED SYNTHESIS OF 2,3 DIMETHYL, 14 HEXA-DI-ONE



CHAPTER 2

DISCUSSION

2.1 ANALYTICAL DISCUSSION

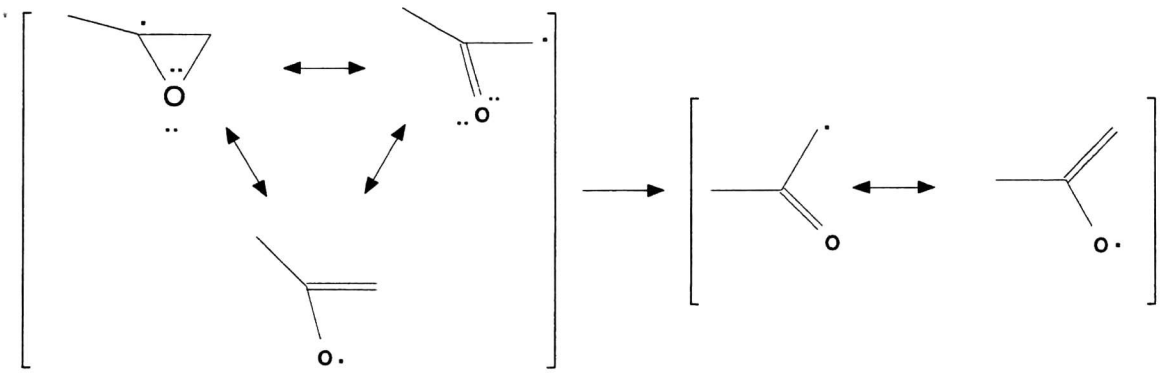
The literature search revealed that 1,4-diketones have been prepared via free radical dehydrodimerization. In that work[4], thermal decomposition of diacetyl peroxide generated methyl free radicals, a hydrogen abstracting agent. Using purely aliphatic ketones with at least one hydrogen atom at the alpha position to the carbonyl group, this technique provides dimers in good yield. For alkyl phenyl ketones with the phenyl group directly attached to the carbonyl, this technique failed to provide 1,4-diketones.

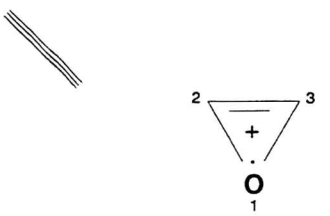
Information involving the behavior of free radicals formed by removal of hydrogen atoms from acids[6], esters[7], nitriles[8], acid halides[7], alkylbenzenes and ring substituted alkylbenzenes[9] has been reported. It has been reported that phenacyl (=benzoylmethyl) radicals generated at 125°C through this technique have never dimerized to form dibenzoyl ethane. It was reported that the intermediate phenacyl radical, if it exists, does not have the classical structure which should lead to dimerization rather, it must have a structure that reduces the electron spin density at the alpha carbon. Evidence later reported[1b,2,3] indicated that phenacyl radical was generated but, that the failure to dimerize was due to the delocalised, non classical nature of its structure.

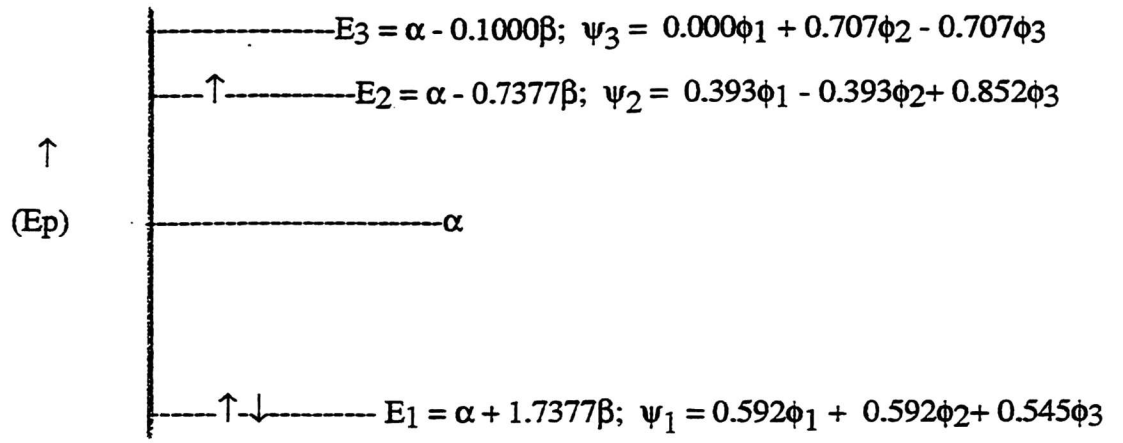
Other reports[3] were given on the study of phenacyl radical generated by photolysis and pyrolysis of phenacyl iodide. In the report, the normal structure of phenacyl radical was produced through pyrolysis at 500°C and it ultimately resulted in formation of benzyl radicals. Furthermore, its known that benzyl radicals, under these conditions, do not dimerize.

Earlier, McBay and co-workers proposed[1a] that benzoylmethyl radical would rearrange to generate styrene epoxidyl radical. They proposed that this would happen because benzoylmethyl radical has higher potential energy than styrene epoxidyl radical. However, this research suggests that styrene epoxidyl radical has a higher potential energy than benzoylmethyl radical, thus, styrene epoxidyl radical should rearrange to benzoylmethyl radical and ultimately bibenzyl should be produced.

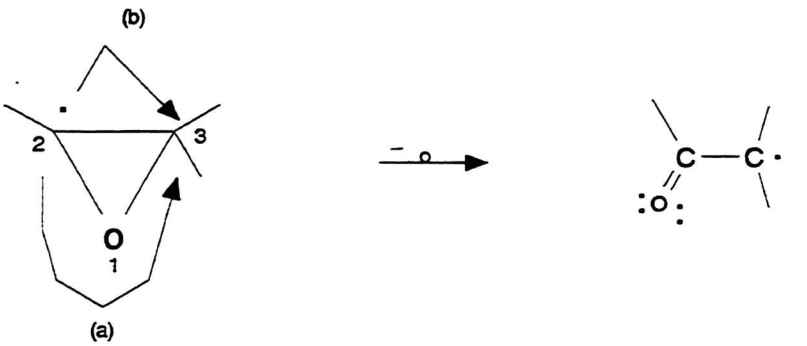
The initial approach in this study has was to develop facile methods to generate this epoxidyl free radical. To do this, the structure of the compounds involved were examined to determine the sequence in which the epoxide bonds would homolitically cleave under stress. Molecular orbital and potential energy calculations were used for this purpose because they give insight into the stability and reactivity of chemical bonds and have been used successfully to predict feasibility and stereochemical course for several classes of organic reactions. The contributions of each canonical form was calculated and recorded as follows:







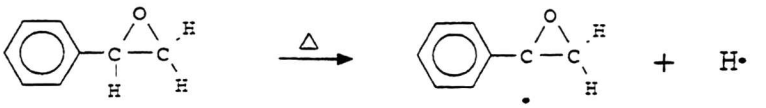
It was concluded from these calculations on the postulated transition state that the reaction path would proceed as indicated by the diagram below for reaction path "a" rather than that of path "b" because the coefficient at position 3 in the wave function depicting the SOMO is by far the larger among all the coefficients.

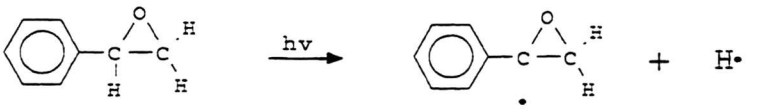


See appendix page 40, for the details of this simple Huckel calculation.

Recent theoretical calculations of a much more sophisticated nature on the ring opening of oxiranes are consistent with our findings. The reaction of oxirane ring opening leads to the formation of intermediates which are detectable via their 1,3-dipolar cycloaddition reactions with unsaturated systems[12-48]. These studies indicate that photolysis, pyrolysis and photobromination were the most suitable methods of approach

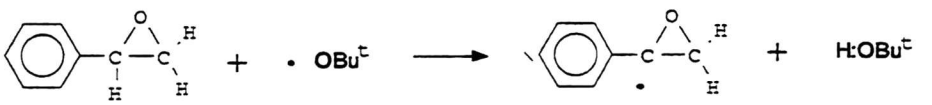
for synthesis of this epoxidyl free radical. The methods initially considered have been the following:

1. 

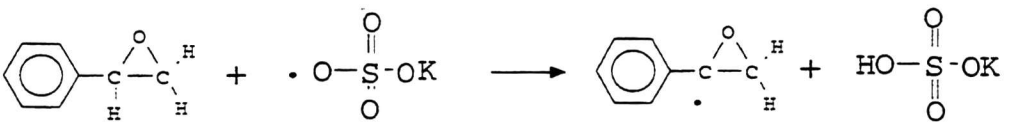
2. 

3. 

4. 

5. 

6. 

7. 

2.2 EXPERIMENTAL DISCUSSION

Included in this report are the preliminary findings regarding approaches 1 through 3, while approaches 4 through 7 are under investigation in this laboratories. In approach 1, pyrolysis of styrene oxide, the required sample was introduced in a cylindrical reservoir bubbled with nitrogen gas while heated on an oil bath at 200°C. The entrained vapors were passed through a McDaniel tube heated at 600°C, after which the product materials were collected and vacuum distilled at reduced pressure. The purity of product was achieved through several recrystallizations of crystals formed from the heavy oil obtained after vacuum distillation.

In approach 2, photolysis of styrene oxide, the sample dissolved in solvent hexane or benzene, was irradiated for three hours and thirty minutes. After irradiation, the solvent was removed and the product material was partially purified by vacuum distillation at reduced pressure. Purity was not attained by distillation, rather, prolonged distillation resulted in further decomposition of collected product material such that chromatographic technique was used to achieve complete separation and purity of product. It was observed that irradiation beyond three hours thirty minutes caused decomposition of product while irradiation for less than three hours would not yield sufficient product.

In approach 3, the sample was heated and photolysed at the same time. A solution containing bromine (6.7g), dissolved in carbon tetrachloride (50ml), was added to a solution of styrene oxide (15ml) dissolved in carbon tetrachloride (100ml) while it was magnetically stirred and white light applied to the system. After complete reaction, the mixture was washed with a 10% solution of, sodium thiosulfate, and water and then dried over sodium sulfate. The solvent was later removed with a roto vapor and the remaining product was purified by vacuum distillation at reduced pressure. Approaches 1 and 2

yielded the expected product bibenzyl while, approach three did not yield bibenzyl, rather, polymeric styrene was obtained.

For the reaction of 2,3 epoxy butane, a similar approach of photolysis did not yield the expected product but pyrolysis at 500°C indicated only traces of the expected product in a mixture of other materials. It was therefore concluded that the optimum conditions necessary for attaining the desired product from 2,3 epoxy butane would not be approach 1 or 2.

CHAPTER 3

EXPERIMENTAL DESCRIPTION

3.1 DESCRIPTION OF PYROLYSIS APPARATUS

The required sample was placed in a 50ml cylindrical Pyrex vessel equipped with a side-arm delivery tube. Inserted into the sample vessel was a tube for bubbling nitrogen gas through the system to entrain the volatile sample. The entrained vapors were passed through a McDaniel tube with a reduced end and a length of 24" (64cm). Approximate I.D by O.D is 7/8" by 11/8" (22 by 29cm). Using an adapter, the reduced end was connected in series to two receiving traps both immersed in dry ice/acetone in a dewar flask. The second receiver was protected with calcium chloride drying tube and connected to water pump for reduced pressure. The McDaniel tube was heated with a Sybron Thermolyne tube furnace, model f21135, at the desired temperature. (See appendix for diagram).

3.2 GENERAL PROCEDURE FOR PYROLYSIS

The purified sample in a Pyrex glass vessel was vaporized by heating on an oil bath or water bath to the desired temperature. Medium aspirator pressure of 25mm was applied while passing nitrogen gas through the system to entrain the volatile sample. The evaporated sample was passed through a McDaniel tube heated at the desired temperature. After evaporation for the required time, the product was collected from the receiver and dissolved in acetone. Acetone was later removed by roto-evaporation, and the product was vacuum distilled for separation and purification. The separated products

were collected, analysed, characterized and identified. $H^1$and C^{13} NMR, IR, and G.C.\MS data have been recorded on these products.

3.3 DESCRIPTION OF PHOTOLYSIS APPARATUS

Photolysis was performed in a hemi-spherical cylindrical quartz glass cell. This has an I.D of 7.0mm, O.D of 8.0mm and thickness of 1.0mm. Inside this cell was a lamp compartment made of quartz, with 7.0 O.D, 4.0 I.D and a water inlet and outlet for cooling the cell. The quartz cell was irradiated from the center by a Hanovia high pressure mercury arc lamp of 450 watt. This lamp operates on a 120 volt, 60 hertz electrical source. A reflux condenser with calcium chloride drying tube was connected to the arm of the quartz vessel to avoid evaporation of solvent, while the solution was stirred with a magnetic stirrer. The experiment was performed in an Ace photochemical safety cabinet.

3.4 GENERAL PROCEDURE FOR PHOTOLYSIS

The solution of sample and solvent was irradiated for three hours and twenty minutes. After irradiation, the solution was collected, the solvent was removed via roto vapor, and the collected product was vacuum distilled. The product was either purified before analysis or it was purified, identified and then characterized. For products that needed further purification, as well as those which decomposed upon distillation at reduced pressure chromatographic technique was used for the separation. Thus, the products were separated and purified after thin layer chromatography by using the chromatotron. After separation, products were analyzed, identified and characterized.

3.5 GENERAL PROCEDURE FOR PHOTOBROMINATION

A sample of purified styrene oxide dissolved in 100ml of carbon tetrachloride was placed in a 500ml three neck flask fitted with a condenser. The required amount of bromine dissolved in 50ml of carbon tetrachloride in a dropping funnel was also introduced into the flask. A rubber tubing with one end fitted to the condenser and the other immersed in water was used for observing and collecting hydrogen bromide and hydrogen gas released during the reaction. White light was generated by a 250 watt incandescent bulb while the apparatus was surrounded with aluminum foil such that the light was contained around the flask. As the solution in the flask was magnetically stirred, light was applied and the bromine solution was allowed to drop into the flask. The system was irradiated with exposure intervals of two minutes on and, two minutes off at the onset. As the reaction proceeded these intervals were increased to five minutes until the bromine was completely added. Irradiation was continued for an additional fifteen minutes until gas was no longer evolved. The contents of the flask were extracted three times, with three separate portions of 10% sodium bicarbonate, 10% sodium thiosulfate and water. They were dried with calcium sulfate and later with molecular sieves for several hours. After drying, the carbon tetrachloride was removed via a roto vapor and the product materials were separated by vacuum distillation under reduced pressure.

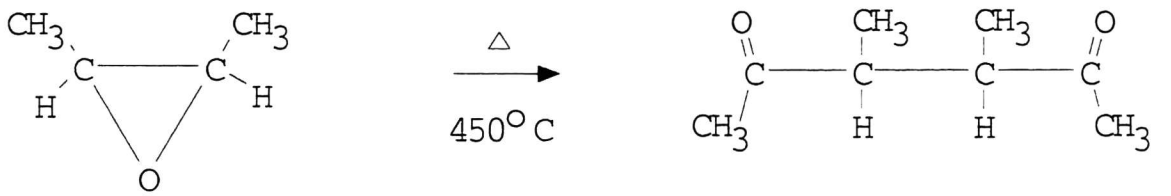
3.6 MATERIALS, SOLVENTS AND PURIFICATION METHOD

Acetone, methanol, carbon tetrachloride, hexane and thiophene-free benzene were purchased from Aldrich Chemicals. Hexane and benzene were purified by passing through a silica gel column, reflected for two hours thirty minutes over molecular sieves and then distilled. Hexane distilled at 68.5-69°C while benzene distilled at 80°C. Boiling point, G.C.\MS, IR, and NMR of both solvents indicated no impurities. Acetone, methanol, carbon tetrachloride were used as purchased. Styrene oxide, and 2,3 epoxy butane were also purchased from Aldrich Chemicals. Styrene oxide was purified by distillation at reduced pressure of 3mm and temperature of 48.5-49.0°C. This corresponds to corrected temperature of 194°C, which is the normal boiling point of styrene oxide. Cyclohexene oxide was distilled at 129-130°C, which also corresponds to the boiling point of cyclohexene oxide. The G.C.\MS, IR and NMR spectra of both samples indicated purity. The 2,3 epoxy butane was used as purchased.

CHAPTER 4

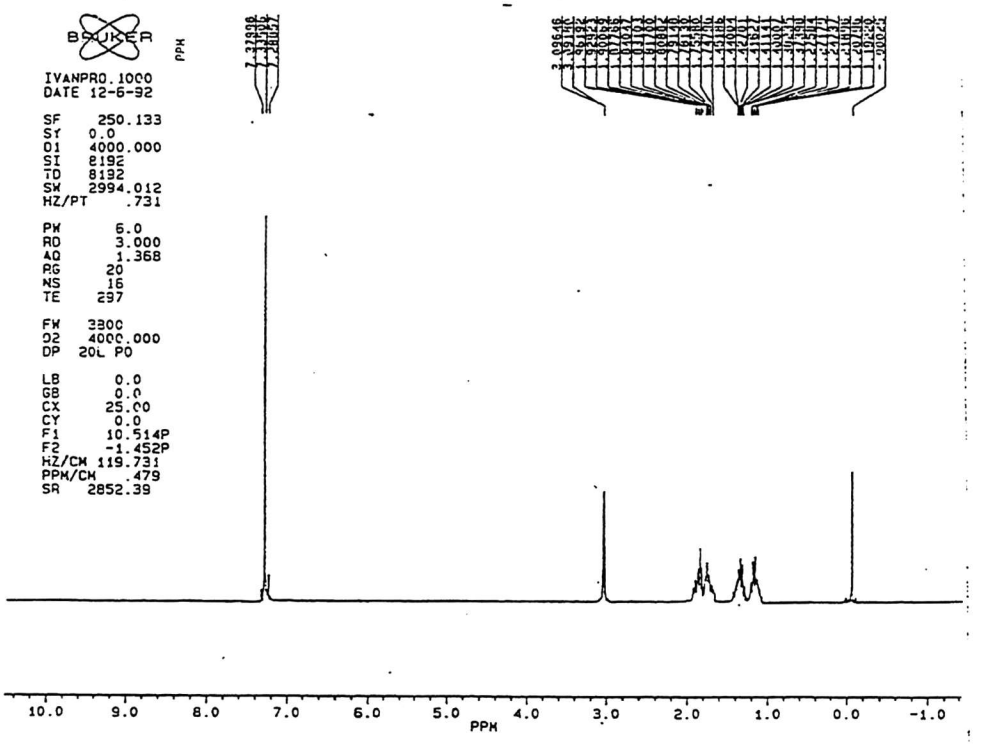
EXPERIMENTS AND RESULTS

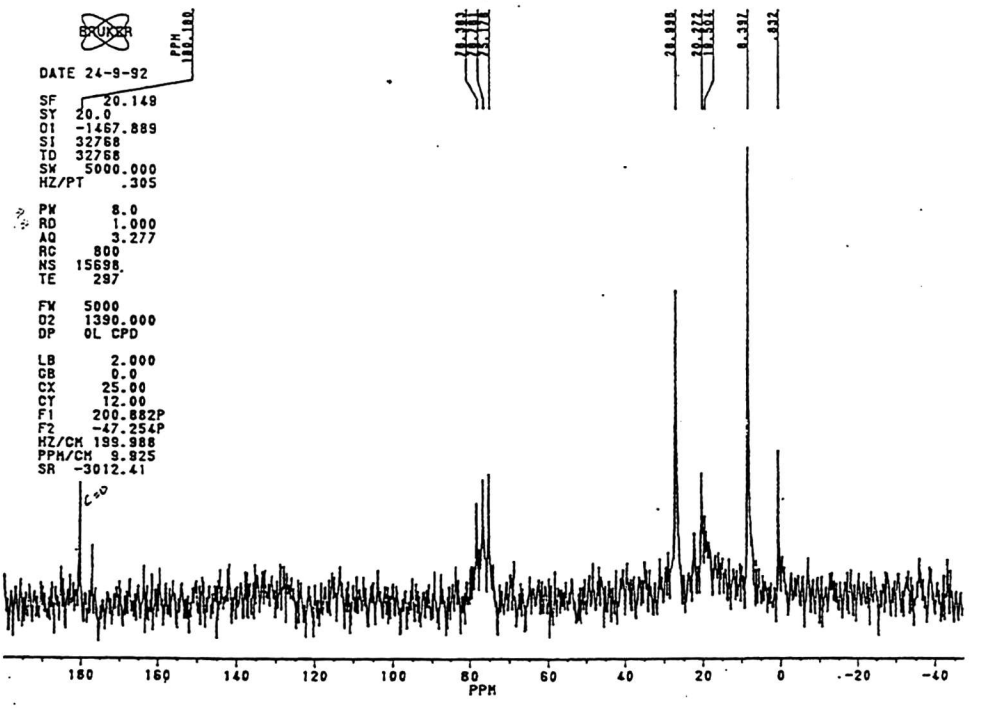
4.1 PYROLYSIS OF 2,3 EPOXY BUTANE



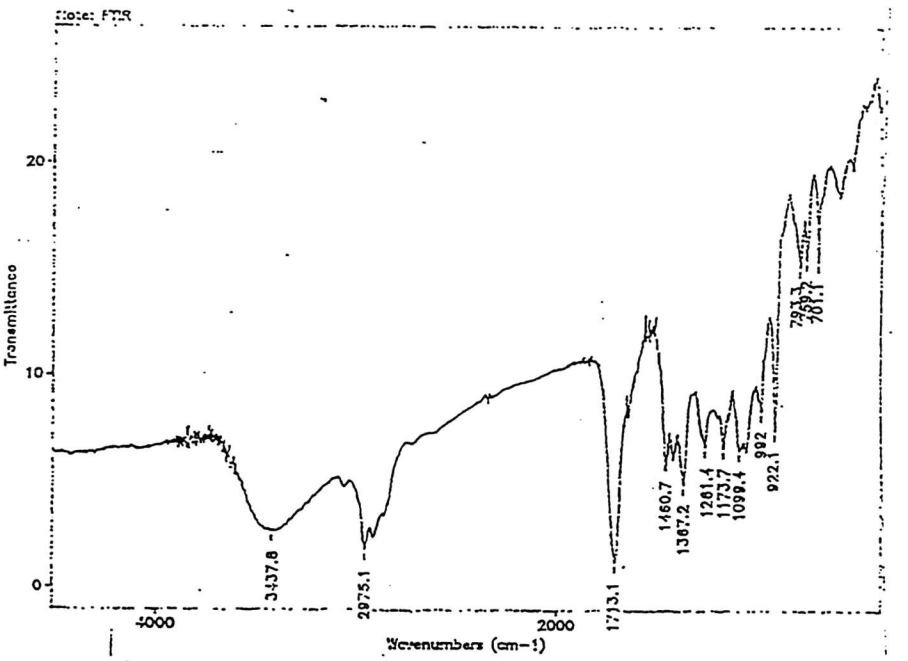
A 15g sample of cis 2,3 epoxy butane in a cylindrical reservoir was evaporated on a water bath of 90°C. The vapor was entrained through a McDaniel tube heated at 450°C. After forty five minutes of evaporation, 1.4g of unevaporated sample was collected from the reservoir while 12.9g of evaporated sample was collected from the receiver. The product was distilled at atmospheric pressure. A fraction, 12g product, was collected at 57-60°C and approximately 0.5g of yellow liquid was recovered from the distillation pot. Both products were analyzed, identified and characterized. The first fraction was identified as the starting material and the material left in the distillation pot was a mixture, possibly containing traces of the expected product 3,4 dimethyl 2,5 hexane-di-one included in pyrolytic resinous gel. Attempts to isolate this product were unsuccessful. See spectra below for obtained results and section on general procedure for details on pyrolysis.

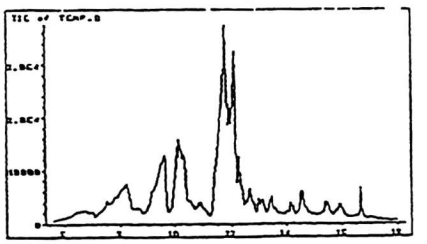
H^1 AND C^{13} OF PYROLYSIS OF 2,3 EPOXY BUTANE





IR AND GC\MS OF PYROLYSIS OF 2,3 EPOXY BUTANE





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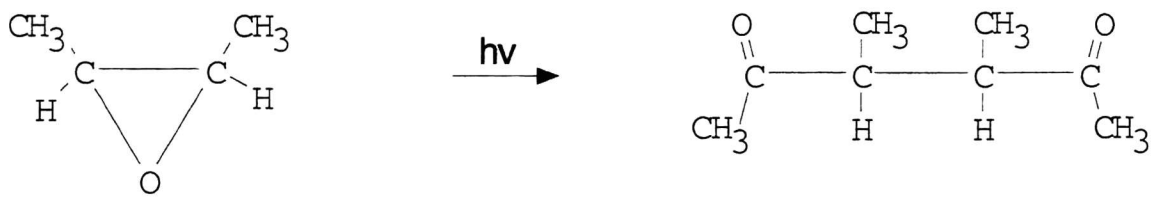
45.0S	387	65.0S	38	82.1S	200	102.1S	78
50.0S	69	66.2S	24	83.1S	100	103.1S	66
51.0S	98	67.1S	353	85.1S	2842	114.2S	29
52.0S	48	68.2S	24	86.1S	181	123.2S	24
53.0S	185	69.1S	185	87.1S	78	124.1S	66
54.1S	67	70.0S	55	88.1S	39	126.1S	17
55.0S	354	71.0S	178	89.0S	32	127.1S	70
56.1S	218	72.1S	566	95.1S	18	131.1S	16
57.1S	766	73.1S	78	97.1S	18	142.2S	383
58.0S	48	74.0S	26	98.1S	13	143.1S	30
59.0S	31	75.1S	26				

Scan 335 (12.086 min) of TEMP.D

X: Scan 310 (11.596 min) of T

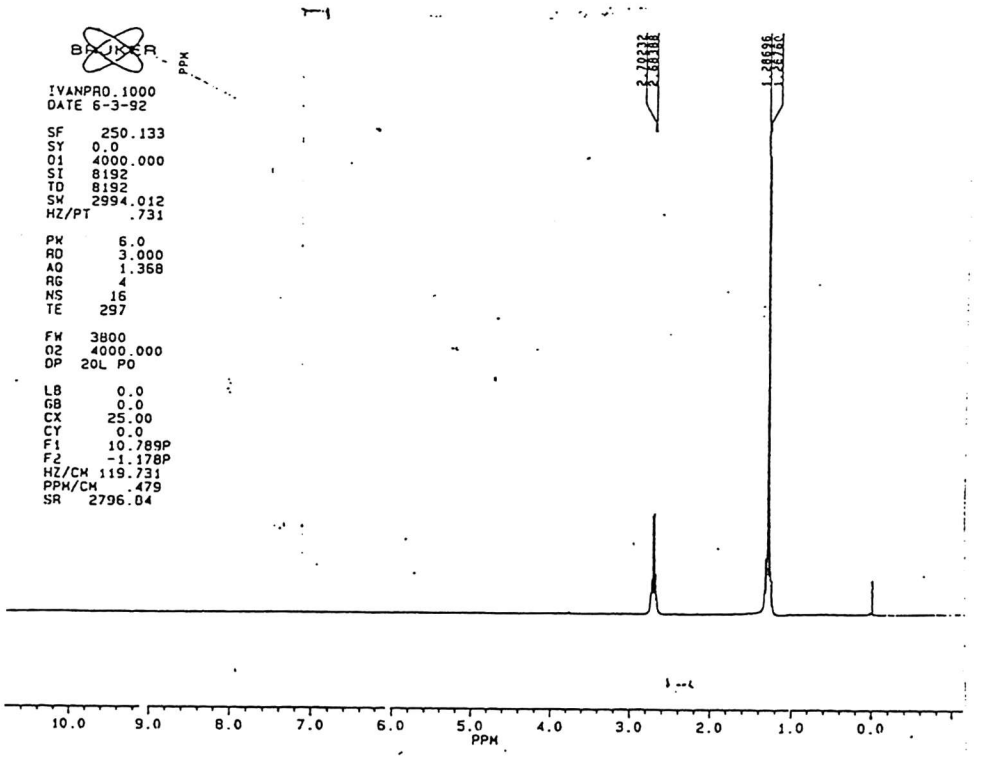
m/z	abund.	m/z	abund.	m/z	abund.	m/z	abund.
41.0S	1072	62.0S	31	80.0S	26	100.1S	1898
43.0S	14271	63.0S	54	81.1S	283	101.1S	123
44.0S	374	64.1S	17	82.1S	324	102.1S	32
45.0S	262	65.0S	128	83.1S	130	103.1S	309
47.1S	28	66.0S	29	85.1S	3150	110.0S	28
50.0S	123	67.0S	349	86.1S	205	114.1S	37
51.0S	159	68.0S	39	87.1S	31	115.1S	20
52.0S	56	69.0S	121	88.1S	27	116.1S	17
53.0S	382	70.1S	54	89.1S	46	120.1S	75
54.0S	70	71.1S	221	91.1S	323	122.2S	22
55.0S	457	72.1S	997	92.1S	68	123.1S	74
56.1S	336	73.1S	67	93.2S	22	124.1S	201
57.1S	675	74.1S	23	95.0S	34	125.2S	27
58.1S	75	75.0S	47	96.2S	21	127.1S	96
59.0S	39	77.0S	65	98.1S	18	142.2S	456
60.0S	16	79.1S	138	99.1S	403	143.2S	44
61.1S	44						

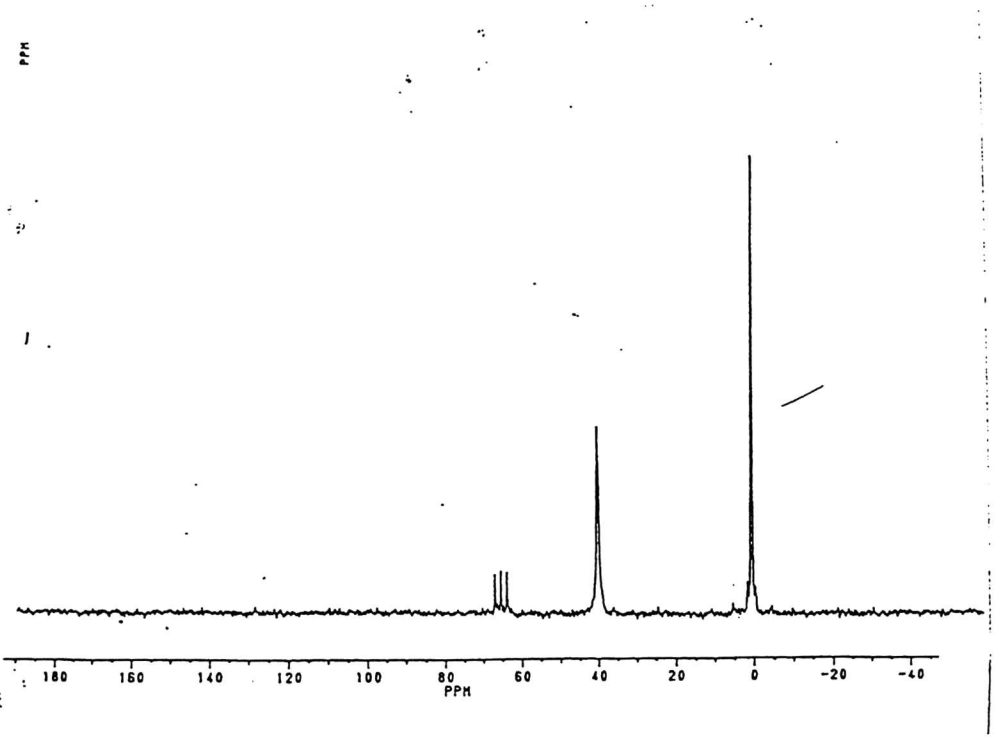
4.2 PHOTOLYSIS OF 2,3 EPOXY BUTANE IN BENZENE



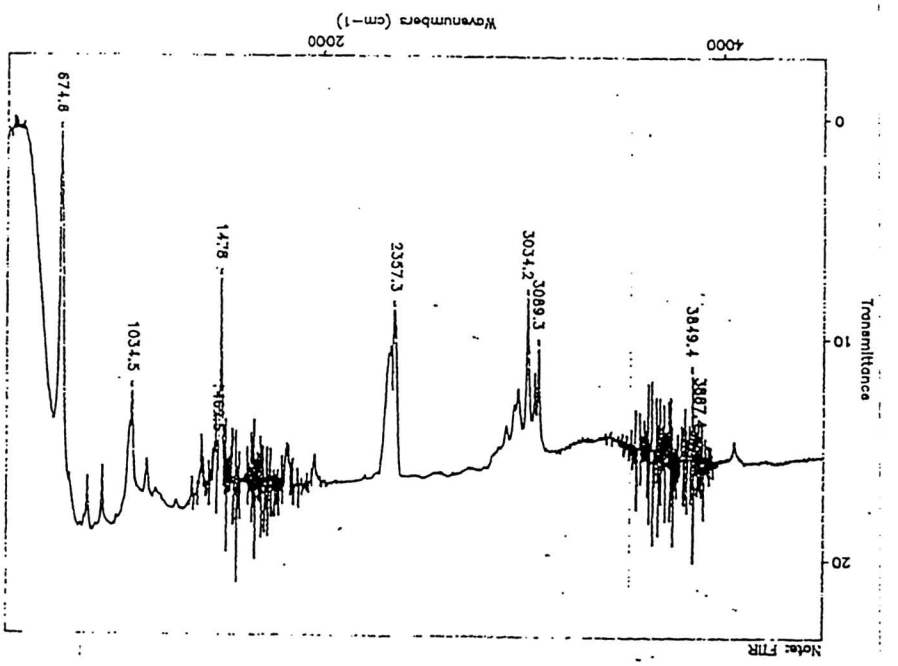
A solution of 15g of cis 2,3 epoxy butane and 140ml thiophene free benzene was magnetically stirred for five minutes in a sample cell. The solution was irradiated for three hours thirty minutes with the 450 watt medium pressure Hanovia arc lamp. After irradiation, the solution was collected and distilled at atmospheric pressure. The first fraction 12.4g of material was collected at 57-61°C and was identified as the starting material. A second fraction 135ml ,was collected at 75-78°C and was identified as benzene. No identifiable photolysis product was obtained. See spectra below for obtained results.

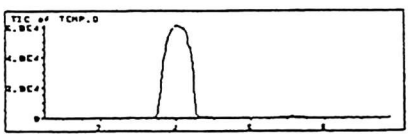
H^1 AND C^{13} PHOTOLYSIS OF 2,3 EPOXY BUTANE IN BENZENE

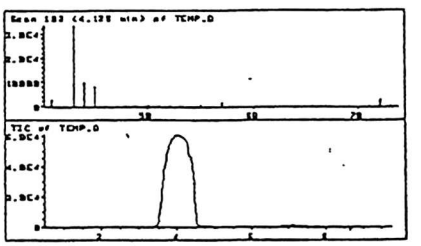




IR AND GC\MS PHOTOLYSIS OF 2,3 EPOXY BUTANE IN BENZENE



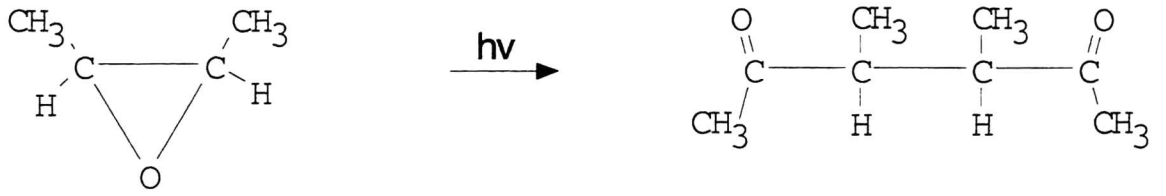




Scan 180 (4.091 min) of TEMP.D

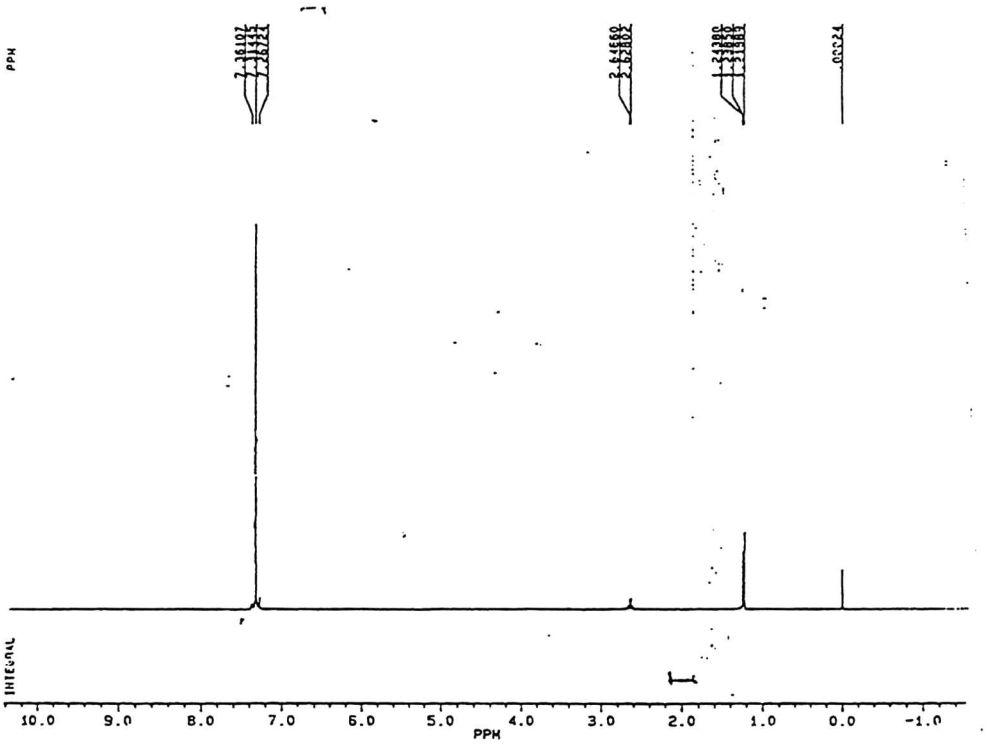
m/z	abund.	m/z	abund.	m/z	abund.	m/z	abund.
41.05	2606	48.15	26	54.00	78	69.00	15
43.05	32496	49.05	159	55.00	352	70.20	19
44.05	10481	50.05	471	56.10	141	71.10	186
45.05	8016	51.05	296	57.00	1244	72.10	2571
46.05	207	52.15	82	58.00	40	73.10	139
47.05	23	53.00	264				

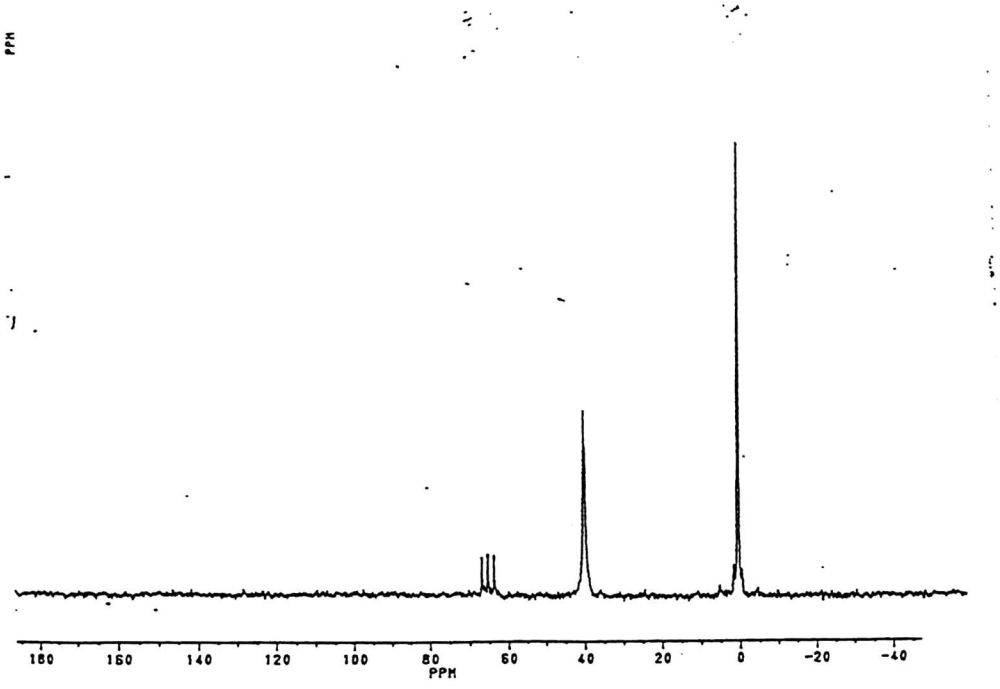
4.4 PHOTOLYSIS OF 2,3 EPOXY BUTANE IN HEXANE



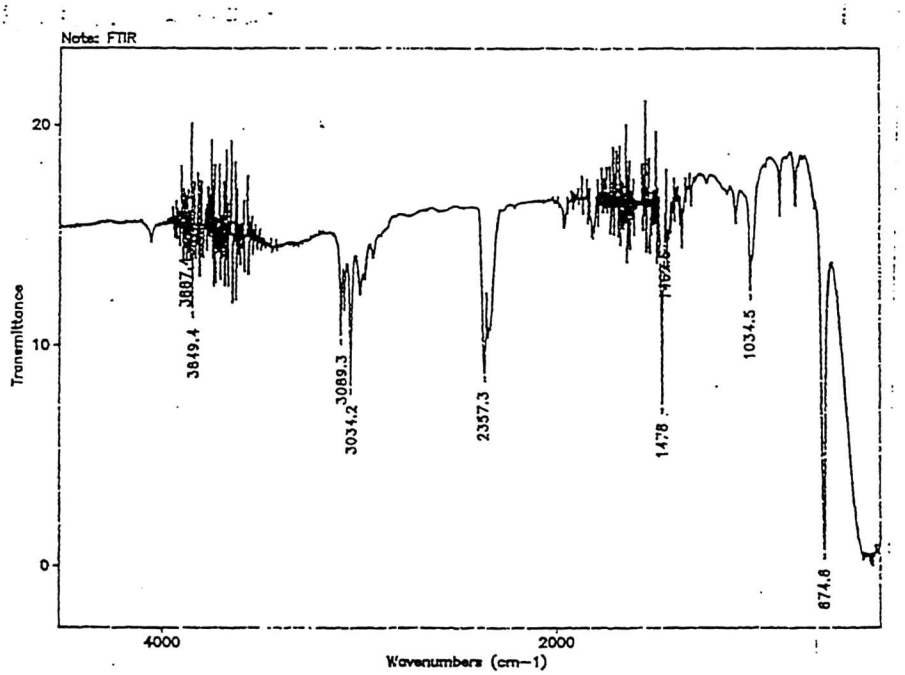
The photolysis of 2,3 epoxybutane was repeated using a solution of 15g sample and 140ml of purified hexane. After irradiation and distillation at atmospheric pressure, 12g of material was collected at 58-62°C and identified as starting material, while 133ml of hexane was recovered at 67-71°C. No identifiable photolysis product was obtained. See spectra below for obtained data.

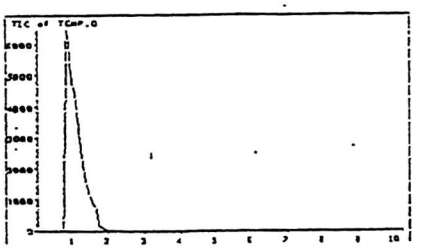
H^1 AND C^{13} PHOTOLYSIS OF 2,3 EPOXY BUTANE IN HEXANE





IR AND GCMS PHOTOLYSIS OF 2,3 EPOXY BUTANE IN HEXANE

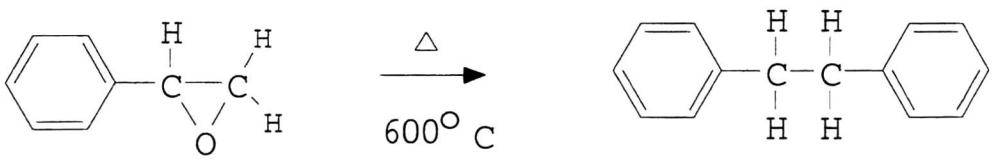




Scan 43 (1.036 min) of TEMP.D

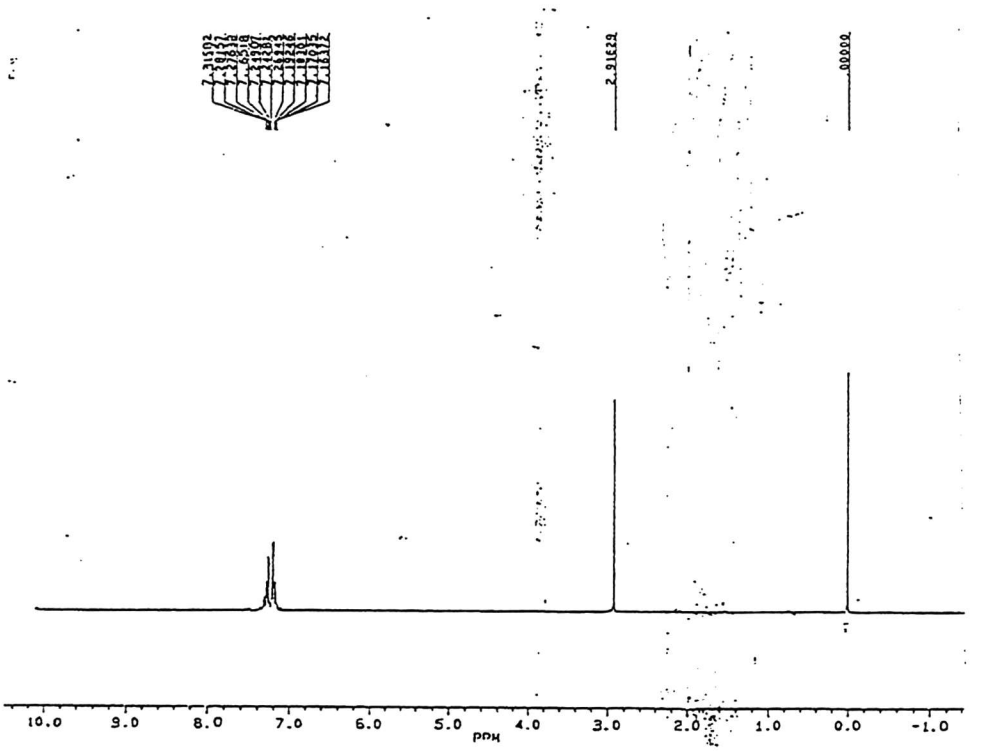
m/z	abund.	m/z	abund.	m/z	abund.	m/z	abund.
41.05	2606	48.15	26	54.00	78	69.00	15
43.05	32496	49.05	159	55.00	352	70.20	19
44.05	10481	50.05	471	56.10	141	71.10	186
45.05	8016	51.05	296	57.00	1244	72.10	2574
46.05	207	52.15	82	58.00	49	73.10	138
47.05	23	53.00	264				

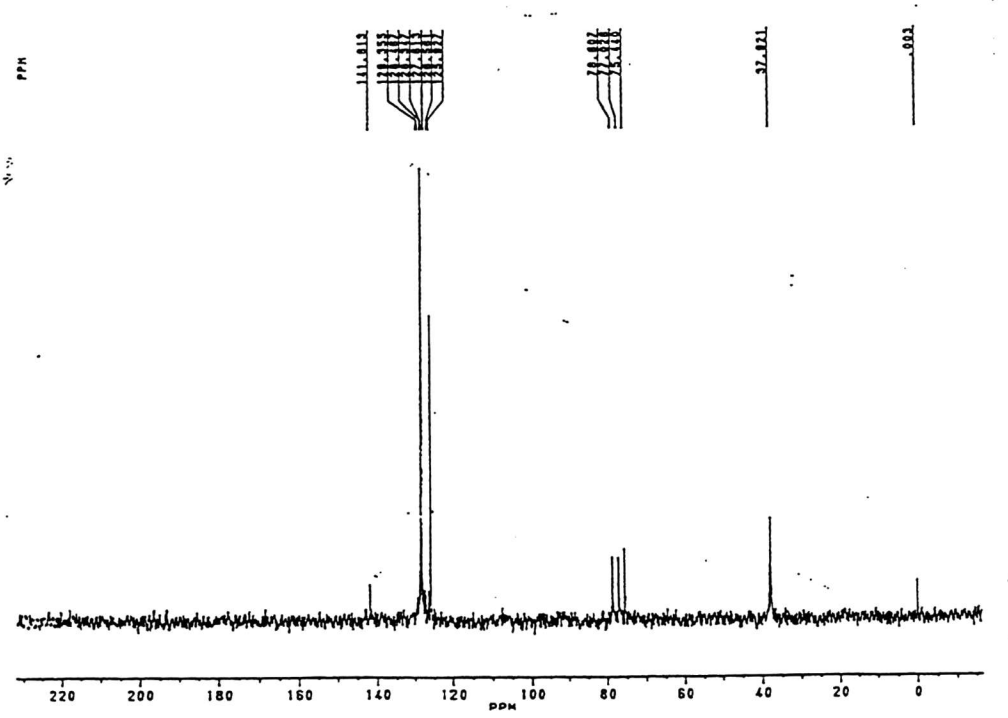
4.4 PYROLYSIS OF STYRENE OXIDE



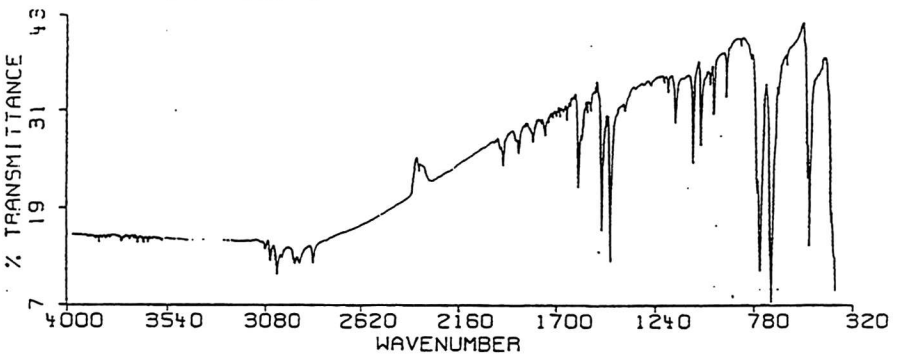
Nitrogen gas was bubbled through a sample of 20ml, (21g, 0.175moles) of styrene oxide contained in a cylindrical reservoir heated on an oil bath at 200°C. These entrained vapors were passed through a McDaniel tube heated at 600°C. After 12 hours of evaporation, 14.5ml of unevaporated sample was collected. The product material was dissolved in acetone and transferred to the distillation apparatus. After the acetone was removed using a roto vapor the residue was vacuum distilled. The first fraction was collected at 60-62°C and at 5mm and was identified as styrene oxide. A second fraction was collected at 136°C and at 5mm, was the expected product, bibenzyl. Upon standing for a two hours at room temperature this yellow material crystallized. Recrystilization was performed several times in methanol and .5g of product was obtained with a melting point of 52 - 53°C. Identification and characterization of this product was attained through GC\MS, IR, and NMR spectroscopic analysis. See spectra below for results and the section on general procedure for further details.

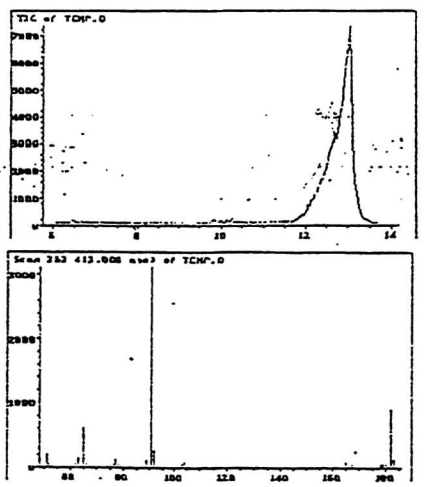
H^1 AND C^{13} PYROLYSIS OF STYRENE OXIDE





IR AND GC\MS PYROLYSIS OF STYRENE OXIDE

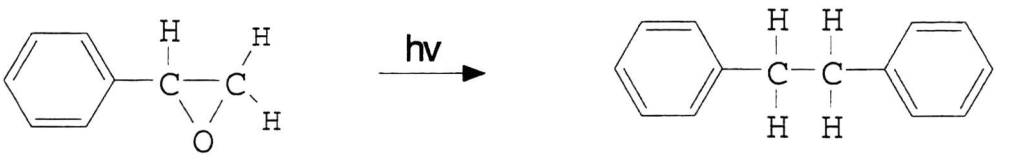




Scan 383 (13.006 min) of TEMP.D

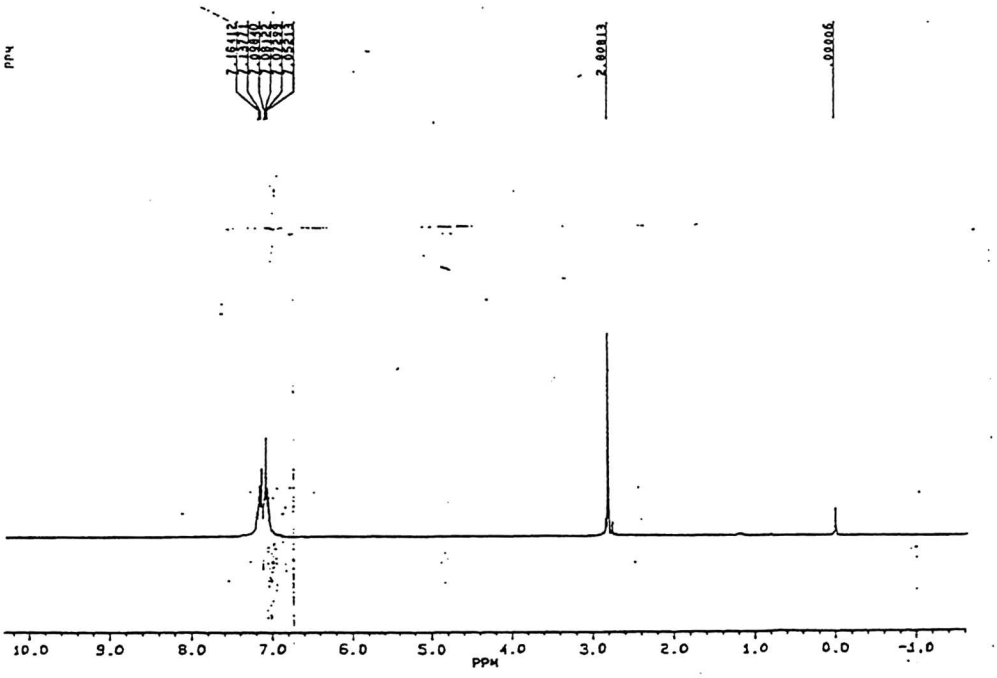
m/z	abund.	m/z	abund.	m/z	abund.	m/z	abund.
51.05	194	74.10	30	92.10	257	178.15	63
52.05	52	76.10	40	103.05	50	179.15	63
62.00	42	77.10	122	104.15	75	180.15	47
63.10	144	78.10	61	165.10	81	182.15	899
65.10	616	89.10	99	157.20	39	183.15	125
66.10	36	91.10	3116	169.20	35		

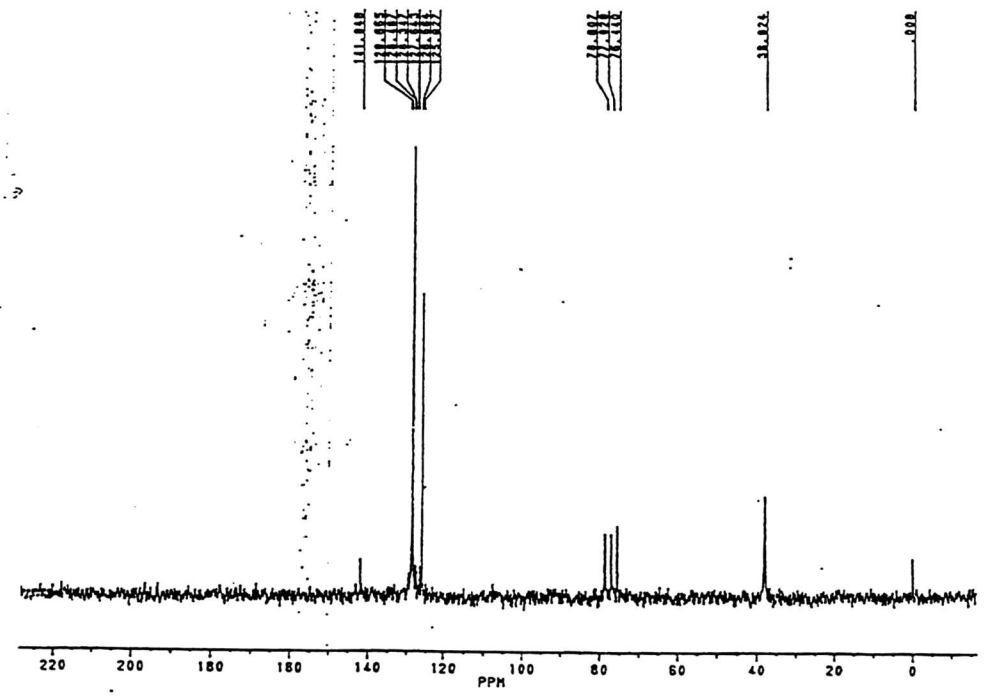
4.5 PHOTOLYSIS OF STYRENE OXIDE IN BENZENE



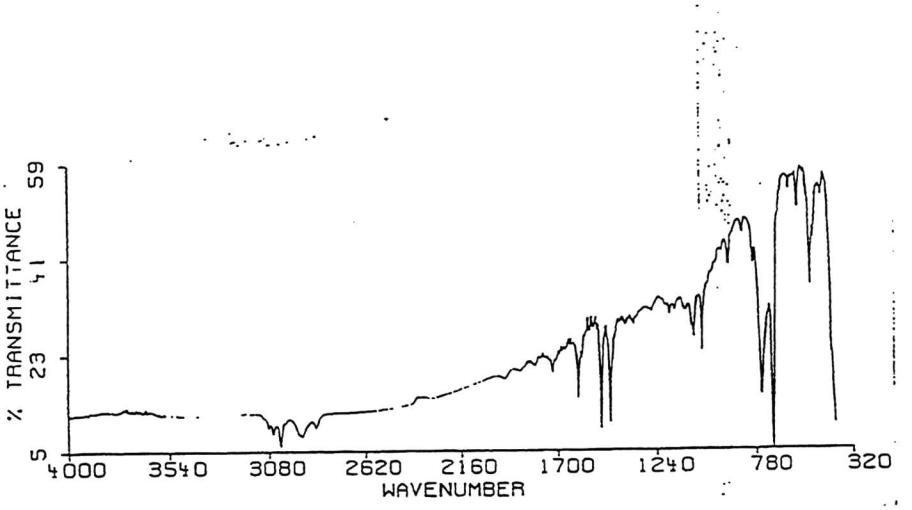
A solution of 33ml of styrene oxide and 120ml thiophene-free benzene was magnetically stirred for five minutes in a sample cell. This solution was irradiated for three hours twenty minutes, using 450 watt medium pressure Hanovia arc lamp. After irradiation, the solution was collected and the solvent, was removed via roto vapor. A 20ml pale yellow material was recovered and distilled at reduced pressure. A fraction, 14.5ml was collected at 5mm and at 60-62°C and 1.4g yellow oily product was collected from the distillation pot. In earlier experiments attempts to purify through distillation resulted in decomposition of product, thus, separation and purification were achieved by chromatography. Thin layer chromatography was performed after the product was dissolved in hexane with a few drops of ethyl acetate. TLC test indicated that the product mixture was made of materials which included the expected product bibenzyl. Chromatotron was used to separate the mixture into three different product fractions. The first product, .35g, was identified as styrene oxide. a second fraction was identified as bibenzyl and the last fraction was identified as a polymeric material. See spectra below for results.

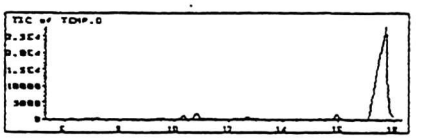
H^1 AND C^{13} PHOTOLYSIS OF STYRENE OXIDE IN BENZENE

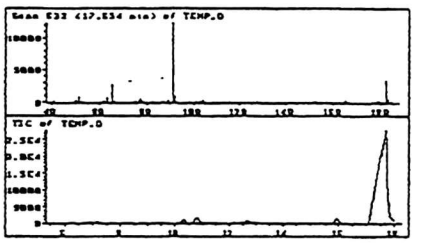




IR AND GC\MS PHOTOLYSIS OF STYRENE OXIDE IN BENZENE



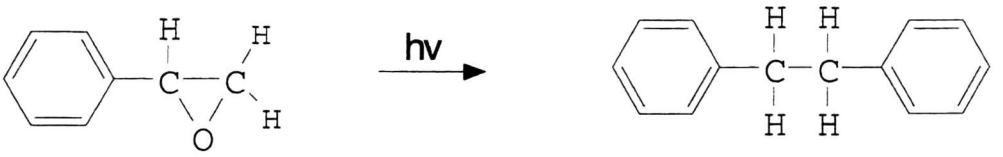




Scan 632 (17.654 min) of TEMP.D

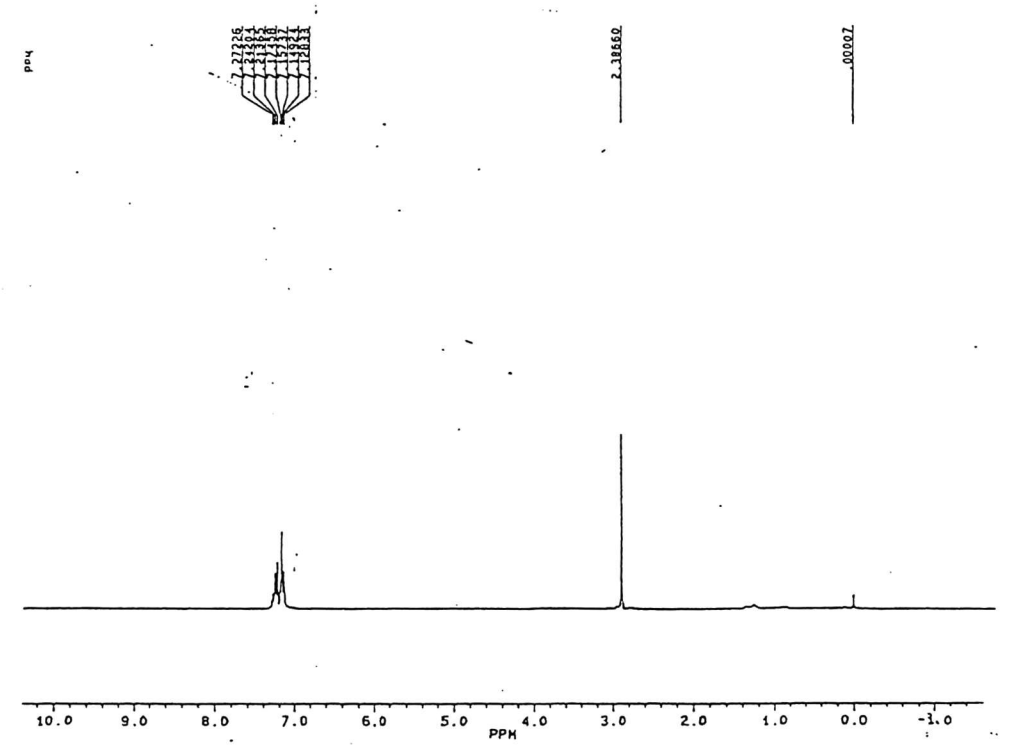
m/z	abund.	m/z	abund.	m/z	abund.	m/z	abund.
41.05	260	78.10	214	104.15	316	153.10	55
50.05	340	79.10	36	105.05	39	154.15	30
51.05	849	82.10	26	113.05	17	165.05	271
52.05	200	86.10	38	115.05	95	166.05	93
53.00	52	87.10	40	116.15	19	167.15	73
61.00	25	88.15	38	126.10	31	176.15	58
62.00	143	89.05	342	127.00	36	177.15	36
63.00	604	91.05	12296	128.10	48	178.15	171
65.10	2627	92.05	907	139.10	39	179.15	108
66.10	135	93.05	31	141.10	24	180.15	45
74.00	97	98.05	20	150.20	34	182.15	3334
75.10	108	101.05	21	151.10	59	183.15	535
76.10	150	102.15	89	152.10	127	184.25	39
77.10	470	103.05	195				

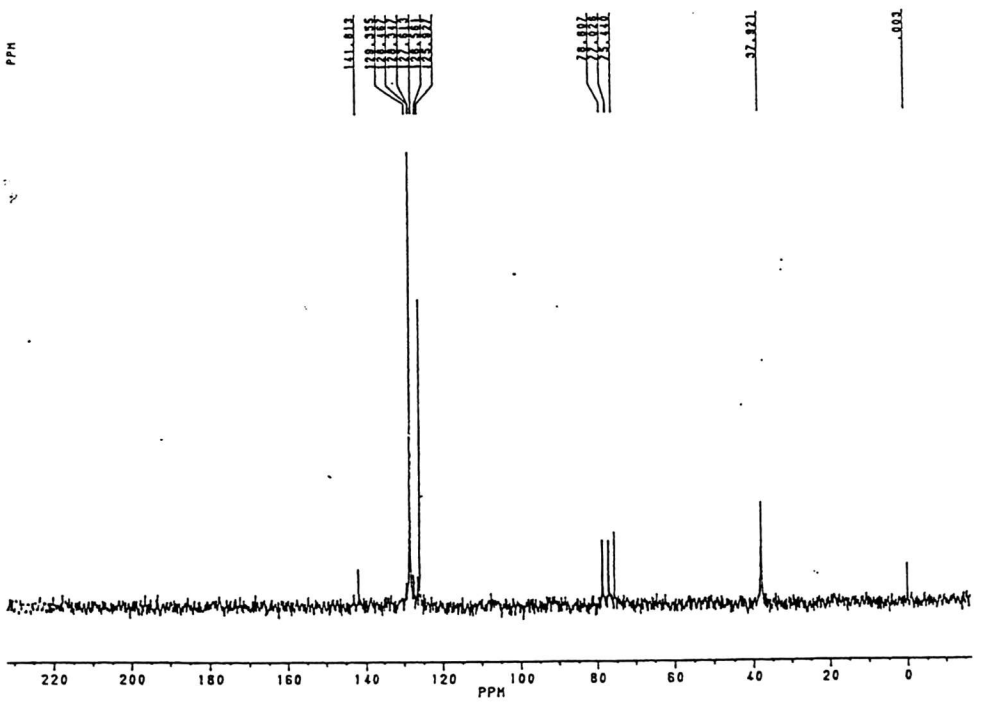
4.6 PHOTOLYSIS OF STYRENE OXIDE IN HEXANE



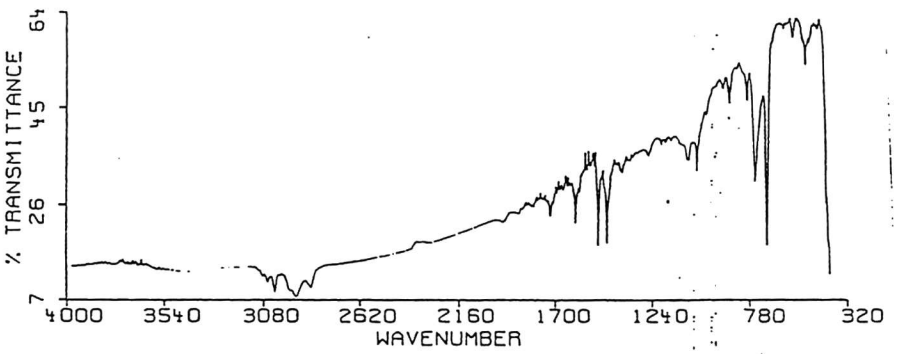
Photolysis of styrene oxide was repeated with a solution of 50ml of sample and 100ml of purified hexane. After irradiation, the solvent was removed, and a product, 36ml, was collected and distilled at reduced pressure. A fraction, 31ml was collected at 4mm and at 54-58° C and identified as styrene oxide. A 3.3ml yellow oily product was collected from the distillation pot and analyzed as in photolysis in benzene. The first fraction, a 0.2g product was collected and identified as styrene oxide. A second fraction, 2.5g was identified as bibenzyl and the last fraction 0.5g was identified as polymeric material. See spectra below for results.

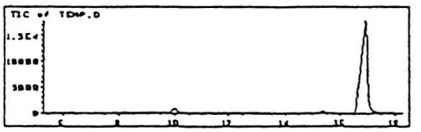
H^1 AND C^{13} PHOTOLYSIS OF STYRENE OXIDE IN HEXANE

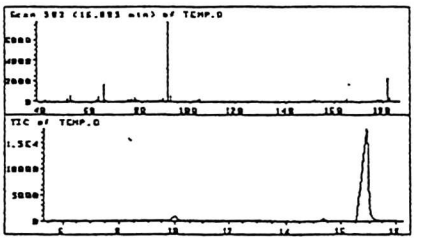




IR AND GCMS PHOTOLYSIS OF STYRENE OXIDE IN HEXANE



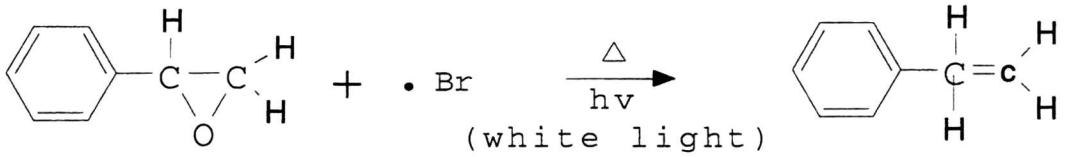




Scan 593 (16.895 min) of TEMP.D

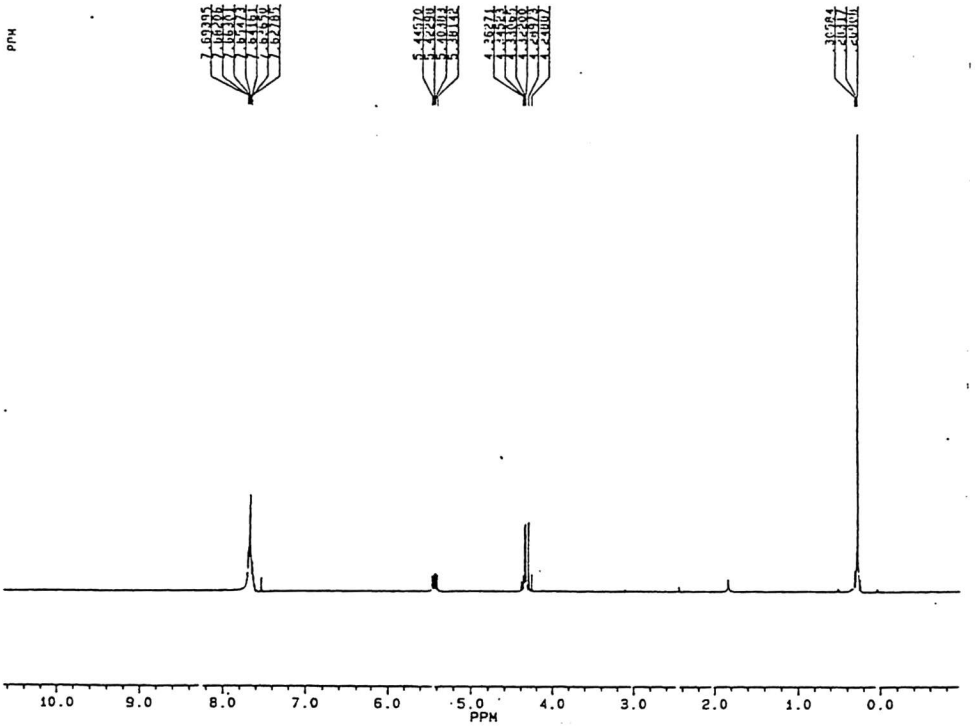
m/z	abund.	m/z	abund.	m/z	abund.	m/z	abund.
41.05	159	77.10	328	101.05	16	153.20	26
42.95	24	78.10	127	102.05	62	164.15	16
50.05	223	79.00	29	103.05	116	165.15	173
51.05	554	82.10	16	104.05	211	166.15	61
52.05	140	82.60	13	105.05	25	167.15	38
53.00	43	86.00	22	115.05	63	176.15	35
62.00	92	87.10	33	126.00	23	177.15	25
63.00	392	88.25	29	127.10	21	178.15	117
65.10	1631	89.05	230	128.10	32	179.15	68
66.00	87	91.05	7781	139.10	24	180.15	23
74.10	71	92.05	557	141.20	14	182.15	2203
75.10	69	93.15	27	151.10	38	183.15	347
76.10	103	97.95	15	152.10	84	184.25	27

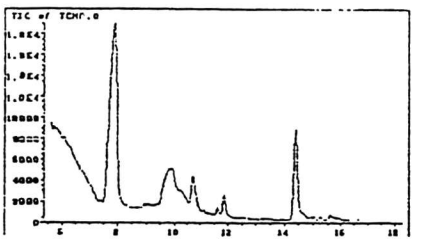
4.7 PHOTOBROMINATION OF STYRENE OXIDE

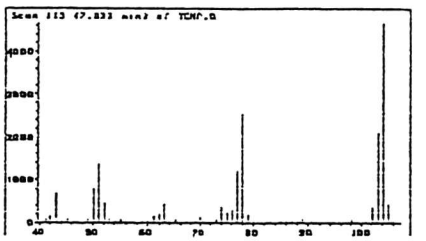


A solution of 15ml styrene oxide dissolved in 100ml carbon tetrachloride was placed in a 500ml three-neck flask fitted with a dropping funnel containing a solution of 6.7ml bromine and 50ml of carbon tetrachloride. Also fitted to the flask was a drying tube and a condenser. The condenser was fitted with a rubber tubing immersed in water, and then to an inverted glass flask for observing and collecting gas bubbles released during reaction. As the solution in the flask was being stirred at room temperature, bromine solution was added dropwise and light was also applied to the flask. Upon addition of bromine, the colorless solution became red and later yellow after complete bromine addition and an extra fifteen minutes of application of light. The contents of the flask were allowed to cool to room temperature. It was then washed three times firstly with 10% sodium bicarbonate, secondly with 10% sodium thiosulfate, and finally with water. It was dried over anhydrous calcium sulfate and the solvent was removed via a roto vapor. Upon standing, the collected yellow product material became greenish and turned later to a brownish color. This was vacuum distilled at reduced pressure (2mm) and the following fractions were collected, fraction one, greenish in color at 92-109°C, fraction two, brownish at 110-112°C, and fraction three a reddish black color at 119-124°C. Fraction one was identified as mostly polymeric styrene and some unreacted styrene oxide. Fraction two and three were identified as decomposed material. It was observed and concluded that heating which is required during distillation causes decomposition of collected product material.

H1 AND GC\MS OF PHOTOBROMINATION OF STYRENE OXIDE







Scan 115 (7.833 min) of TEMP.D

m/z	abund.	m/z	abund.	m/z	abund.	m/z	abund.
41.15	84	55.00	14	73.00	97	88.10	39
42.05	139	57.00	48	74.10	351	89.05	98
43.05	862	60.00	24	75.10	237	97.05	25
44.15	39	61.10	141	76.10	273	98.05	84
45.15	85	62.00	184	77.10	1185	99.05	18
49.05	88	63.00	408	78.10	2516	101.05	44
50.05	813	64.00	45	79.10	182	102.15	363
51.05	1342	65.10	75	80.10	28	103.15	2065
52.15	439	67.20	13	83.10	26	104.15	4652
53.05	81	68.10	26	85.00	16	105.15	417
54.10	37	69.10	45	86.00	19	106.05	31
55.00	99	70.10	107	87.10	35		

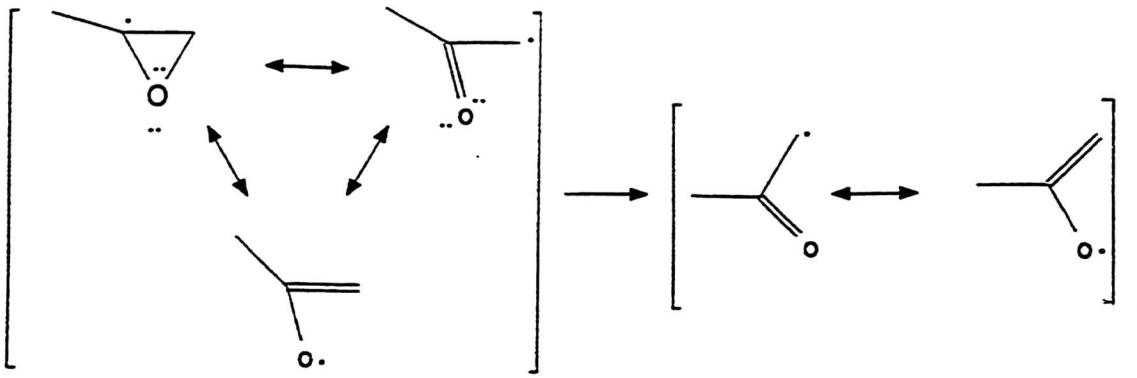
CHAPTER 5

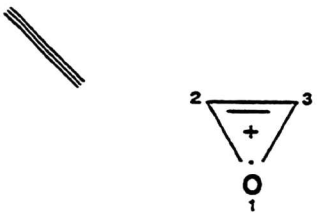
CONCLUSION

Earlier studies demonstrated that the phenacyl radical when generated at elevated temperatures, will rearrange to form benzyl radical[3]. This radical dimerizes to form bibenzyl. In this research, it was demonstrated that through pyrolysis at 600°C and photolysis, the phenacyl radical was generated by the rearrangement of an alpha styrene epoxidyl free radical. This then follows a tested and proven reaction path to form bibenzyl. Photobromination of styrene oxide did not yield phenacyl free radical rather, it resulted to the formation of polymeric styrene. Pyrolysis of 2,3 epoxy butane generated the desired epoxidyl free radical necessary to produce 2,3-dimethyl 1,4-hexa-di-one. However, results obtained from the photolysis of 2,3 epoxy butane indicated that the desired product was not achieved. This system is the subject of further investigations in this laboratory.

APPENDIX

HUCKEL MOLECULAR ORBITAL CALCULATION





$$\begin{vmatrix} \frac{\alpha - E}{\beta} & 0.8 & 0.8 \\ 0.8 & \frac{\alpha - E}{\beta} & 1 \\ 0.8 & 1 & \frac{\alpha - E}{\beta} \end{vmatrix} = 0$$

$$\begin{vmatrix} m & 0.8 & 0.8 \\ 0.8 & m & 1 \\ 0.8 & 1 & m \end{vmatrix} = 0$$

1. $C_1 (H_{11} - ES_{11}) + C_2 (H_{12} - ES_{12}) + C_3 (H_{13} - ES_{13}) = 0$
2. $C_1 (H_{21} - ES_{21}) + C_2 (H_{22} - ES_{22}) + C_3 (H_{23} - ES_{23}) = 0$
3. $C_1 (H_{31} - ES_{31}) + C_2 (H_{32} - ES_{32}) + C_3 (H_{33} - ES_{33}) = 0$

1. $C_1 (\alpha - E) + C_2 (.8\beta) + C_3 (.8\beta) = 0$
2. $C_1 (.8\beta) + C_2 (\alpha - E) + C_3 (.8\beta) = 0$
3. $C_1 (.8\beta) + C_2 (.8\beta) + C_3 (\alpha - E) = 0$

Now; $E_1 = \alpha + 1.7377$, therefore,

1. $C_1 (-1.7377\beta) + C_2 (.8\beta) + C_3 (.8\beta) = 0$
2. $C_1 (.8\beta) + C_2 (-1.7377\beta) + C_3 (.8\beta) = 0$
3. $C_1 (.8\beta) + C_2 (.8\beta) + C_3 (-1.7377\beta) = 0$

From equation 1; we solve for C_1

$C_1 (-1.7377\beta) = - (.8\beta) (C_2 + C_3)$;

$C_1 = - .8\beta (C_2 + C_3)$

$$C_1 = \frac{- .8\beta (C_2 + C_3)}{- 1.7377}$$

$$C_1 = \frac{- .8(C_2 + C_3)}{- 1.7377}$$

Now from equation 11; we solve C_2;

$C_2 = (-1.7377\beta)$

$C_2 = - (.8\beta) (C_1 + C_3)$;

$$C_2 = \frac{- .8(C_1 + C_3)}{-1.7377};$$

$$C_2 = \frac{+.8 (C_1 + C_3)}{1.7377};$$

We now substitute into equation 1, and were $C_1 = f (C_1;C_3)$

The value of C_2 from equation 11.

$$C_1 = \frac{.8\,(C_1 + C_3);}{1.7377}$$

$$C_1 = \frac{.8\,(C_1 + C_3) \quad + \quad (C_3)}{1.7377}$$

Hence:

$$C_1 = \frac{.64C_1 - .8C_3 + .8\,(1.7377C_3)}{(0.7377)^2}$$

$$C_1 = \frac{.64C_1 - .8C_3 + .8\,(1.39016C_3)}{(3.0196013)}$$

$3.0196013C_1 - .64C_1 = .8C_1 + .1.39016\ C_3$

$2.379013 = 2.19016$

$$C_1 = \frac{2.19016}{2.3796013}$$

$C_1 = (0.9203894)C_3$

Now we calculate from equation 111; $C_3 = f(C_1;C_3)$;

$(-1.7377\beta)C_3 = (-)\beta\,(.8C_1 + C_2)$ and

$$C_1 = \frac{+.8(C_1 + C_2)}{1.7377}$$

Substituting for C_3 into equation 1, where $C_1 = f(C_3)$; we get

$$C_1 = 0.9203894 \quad \frac{+\,.8(C_1 + C_2)}{1.7377}$$

$$= 0.5296595\,(.8C_1 + C_2)$$

$$C_1 = 0.423726\, C_1 + 0.5296595\, C_2$$

$$= (0.52296595)\, C_2$$

$$C_1 = \frac{0.5296595}{0.576622724}\, C_2$$

$$C_1 = (.9191131)C$$

$$\text{Now, } C_1; C_2; C_3 = 1; \frac{1}{.91191131}; \frac{1}{0.9203894}$$

$$C_1; C_2; C_3 = 1; 1.0880053; 1.0864967$$

$$\text{Now to normalize } \Psi_1: \frac{1}{\sqrt{\sum C_i^2}}$$

$$= \frac{1}{\sqrt{1^2 + (1.0880053)^2 + (1.0864967)^2}}$$

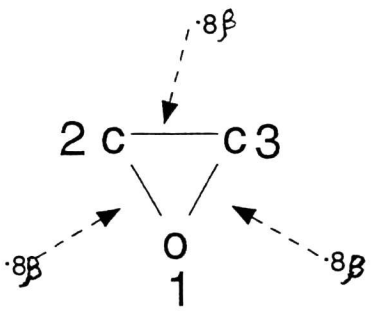
$$= \frac{1}{1.8341839}$$

$$C_1 = 0.5452016 = 1 \times \frac{1}{1.8341839}$$

$$C_1 = 0.5931822 = 1.0880053 \times \frac{1}{1.8341839}$$

$$C_1 = 0.5923597 = 1.0864967 \times \frac{1}{1.8341839}$$

Thus for the nonbonding system;



$\Psi_1 = 0.54520\phi_1 + 0.59318\phi_2 + 0.5923\phi_3$

1. $C_1 (H_{11} - ES_{11}) + C_2 (H_{12} - ES_{12}) + C_3 (H_{13} - ES_{13}) = 0$
2. $C_1 (H_{21} - ES_{21}) + C_2 (H_{22} - ES_{22}) + C_3 (H_{23} - ES_{23}) = 0$
3. $C_1 (H_{31} - ES_{31}) + C_2 (H_{32} - ES_{32}) + C_3 (H_{33} - ES_{33}) = 0$

1. $C_1 (\alpha - E) + C_2 (.8\beta) + C_3 (.8\beta) = 0$
2. $C_1 (.8\beta) + C_2 (\alpha - E) + C_3 (.8\beta) = 0$
3. $C_1 (.8\beta) + C_2 (.8\beta) + C_3 (\alpha - E) = 0$

Now; $E_2 = \alpha - 0.7377$, therefore,

1. $C_1 (0.7377\beta) + C_2 (.8\beta) + C_3 (.8\beta) = 0$
2. $C_1 (.8\beta) + C_2 (0.7377\beta) + C_3 (.8\beta) = 0$
3. $C_1 (.8\beta) + C_2 (.8\beta) + C_3 (0.7377\beta) = 0$

From eqquation 1; we solve for C_1

$C_1 (0.7377\beta) = - (.8\beta) (C_2 + C_3);$

$C_1 = - .8\beta (C_2 + C_3)$

$$C_1 = \frac{- .8 (C_2 + C_3)}{0.7377}$$

$$C_1 = \frac{.8 (C_2 + C_3)}{0.7377}$$

$C_2 (0.7377\beta) = - (.8\beta) (C_1 + C_3);$

$$C_2 = \frac{-.8\beta\,(C_1 + C_3)}{0.7377\beta}$$

$$C_2 = \frac{-.8\,(C_1 + C_3)}{0.7377}$$

Now substituting into 1, for C_2 from 11, we get:

$$C_2 = (-)\,.8\,\frac{-.8\,(C_1 + C_3)}{0.7377} + \frac{C_2}{1}$$

$$\frac{}{0.7377}$$

$$C_1 = \frac{.64C_1 - .8C_3 + .8\,(0.7377C_3)}{(0.7377)^2}$$

$$C_1 = \frac{.64C_1 - .20984C_3}{5442012}$$

$$C_1 = .5442012C_1 - .64C_1$$

$$C_1 = .20984C_3$$

$$.20984C_1 = 0.20984C_3$$

$$C_1 = -2.1904241C_3$$

Now from 111; one solves for $C_3 = f\,(C_1;C_2)$;

$$C_2\,(0.7377\beta) = -\,(.8\beta)\,(C_1 + C_2);$$

$$C_3 = \frac{-\,(.8C_1 + C_2);}{0.7377}$$

Substituting into above C_3 equation for $C_3 = f\,(C_1;C_2)$, so that;

$$C_1 = \frac{(-)\ 2.1904241}{1} - \frac{(-)\ (.8C_1 + C_2)}{0.7377}$$

$$C_1 = (-)\ (2.9692614\ )\ \ (-)\ (.8C_1 + C_2)$$

$$C_1 = \frac{(-)\ (2.9692614\ )}{1.3754091}\ C_2$$

$$C_1 = (-)\ (2.1588205)\ C_2$$

$$\Psi_2 = 1.0\phi_1 + 0.46321\phi_2 + 0.45653\phi_3$$

Now to normalize Ψ_2: $\frac{1}{\sqrt{\Sigma\ C_i^{\,2}}}\ (1.0\phi_1 + 0.46321\phi_2 + 0.45653\phi_3)$

Now, $C_1; C_2; C_3 = 1;\ \frac{1}{2.1588205}\ ;\ \frac{1}{2.1904241}$

$C_1; C_2; C_3 = 1;\ 0.4632159;\ 0.4565326$

$$= \frac{1}{\sqrt{C_1^2 + C_2^2 + C_3}}$$

$$= \frac{1}{\sqrt{1^2 + .2145689 + .208422}}$$

$$= \frac{1}{\sqrt{1.422991}}$$

$$= \frac{1}{1.1928919}$$

Hence $\Psi_2 = \frac{1}{1.1928919}\phi_1 + \frac{1}{1.1928919}\phi_2 + \frac{1}{1.1928919}\phi_3$

$\Psi_2 = 0.8382989\phi_1 - 0.38831323\phi_2 - 0.3827107\phi_3$

Thus $\Psi_2 = -0.8382989\phi_1 + 0.38831323\phi_2 + 0.3827107\phi_3$

1. $C_1 (H_{11} - ES_{11}) = C_2 (H_{12} - ES_{12}) + C_3 (H_{13} - ES_{13}) = 0$
2. $C_1 (H_{21} - ES_{21}) = C_2 (H_{22} - ES_{22}) + C_3 (H_{23} - ES_{23}) = 0$
3. $C_1 (H_{31} - ES_{31}) = C_2 (H_{32} - ES_{32}) + C_3 (H_{33} - ES_{33}) = 0$

1. $C_1 (\alpha - E) + C_2 (.8\beta) + C_3 (.8\beta) = 0$
2. $C_1 (.8\beta) + C_2 (\alpha - E) + C_3 (.8\beta) = 0$

$C_1 (.8\beta) + C_2 (.8\beta) + C_3 (\alpha - E) = 0$

$E3 = \alpha - 1.0000\beta$

1. $C_1 (\alpha - (\alpha - E)) + C_2 (.8\beta) + C_3 (.8\beta) = 0$
2. $C_1 (.8\beta) + C_2 (\alpha - (\alpha - E)) + C_3 (.8\beta) = 0$
3. $C_1 (.8\beta) + C_2 (.8\beta) + C_3 (\alpha - (\alpha - E)) = 0$

1. $C_1 (\beta) + C_2 (.8\beta) + C_3 (.8\beta) = 0$

11. $C_1 (.8\beta) + C_2 (\beta) + C_3 (.8\beta) = 0$

111. $C_1 (.8\beta) + C_2 (.8\beta) + C_3 (\beta) = 0$

1. $C_1 (\beta) = .8\beta (C_2 + C_3)$;

and $C_1 = \dfrac{.8 (C_2 + C_3)}{\beta} = (-) .8 (C_2 + C_3)$

11. From 11; we now solve for $C_2 = f (C_1 + C_3)$;

$C_2 (\beta) = (-) (.8\beta C_1 + C_3)$;

$C_2 = \dfrac{(-)\beta (.8 C_1 + C_3)}{\beta}$;

$C_2 = \dfrac{(-) (.8 C_1 + C_3)}{1}$;

Now substituting into 1; we get:

$C_1 = (-) .8 (- (.8 C_1 + C_3)) = (.64C_1 - .8C_3 - .8C_3) = .64C_1$

$(C_1 - .64C_1) = 0$; $.36C_1 = 0$; $C_1 = 0$

1. $C_1(\beta) + C_2(.8\beta) + C_3(.8\beta) = 0$
11. $C_1(.8\beta) + C_2(\beta) + C_3(.8\beta) = 0$
111. $C_1(.8\beta) + C_2(.8\beta) + C_3(\beta) = 0$

$$C_2 = \frac{(-)\beta(.8\,C_1 + C_3)}{\beta} = (-).8\,(C_2 + C_3) = -.8\,C_2 - .8\,C_3$$

11. From 11; we now solve for $C_2 = f(C_1\,C_3)$;

$C_2(\beta) = (-)(.8\beta\,C_1 + C_3)$;

$$C_2 = \frac{(-)\beta(.8\,C_1 + C_3)\,;}{\beta}$$

$$C_2 = \frac{(-)(.8\,C_1 + C_3)\,;}{1} = -.8\,C_1 + .8\,C_3$$

Now substituting into 1; we get:

$C_1 = (-).8(-(.8\,C_1 + C_3) + C_3)$

$C_1 = (-).8(-.8\,C_1 - C_3 + C_3)$

$C_1 = +.64C_1$

$C_1 - .64C_1 = 0$; $.36C_1 = 0$; $C_1 = 0$

Now $C_1 = 0$ thus from 111; $C_2(\beta) = -C_3(\beta)$ and $C_2 = -C_3$

$\Sigma C_i^2 = 1$;

Hence; $C_1 = 0$; $C_2 = .707$; $C_3 = -.707$

Hence; $\Psi_1 = 0C_1 + .707C_2 - .707C_3$

FIGURE 1

POTENTIAL ENERGY PROFILE FOR THE REARRANGEMENT OF EPOXIDYL FREE RADICAL GENERATED FROM STYRENE OXIDE

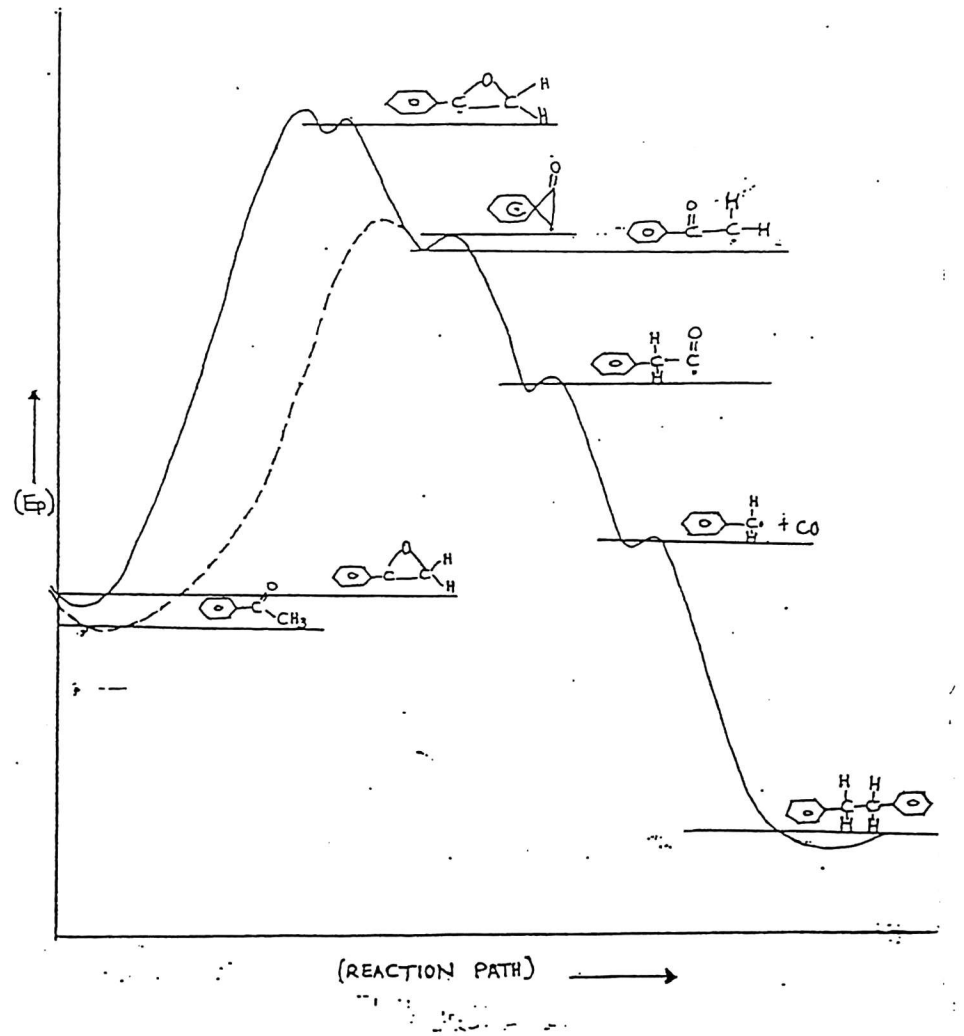


FIGURE 2

POTENTIAL ENERGY PROFILE FOR THE ATTEMPTED SYNTHESIS OF 2,3 DIMETHYL, 14 HEXA-DI-ONE

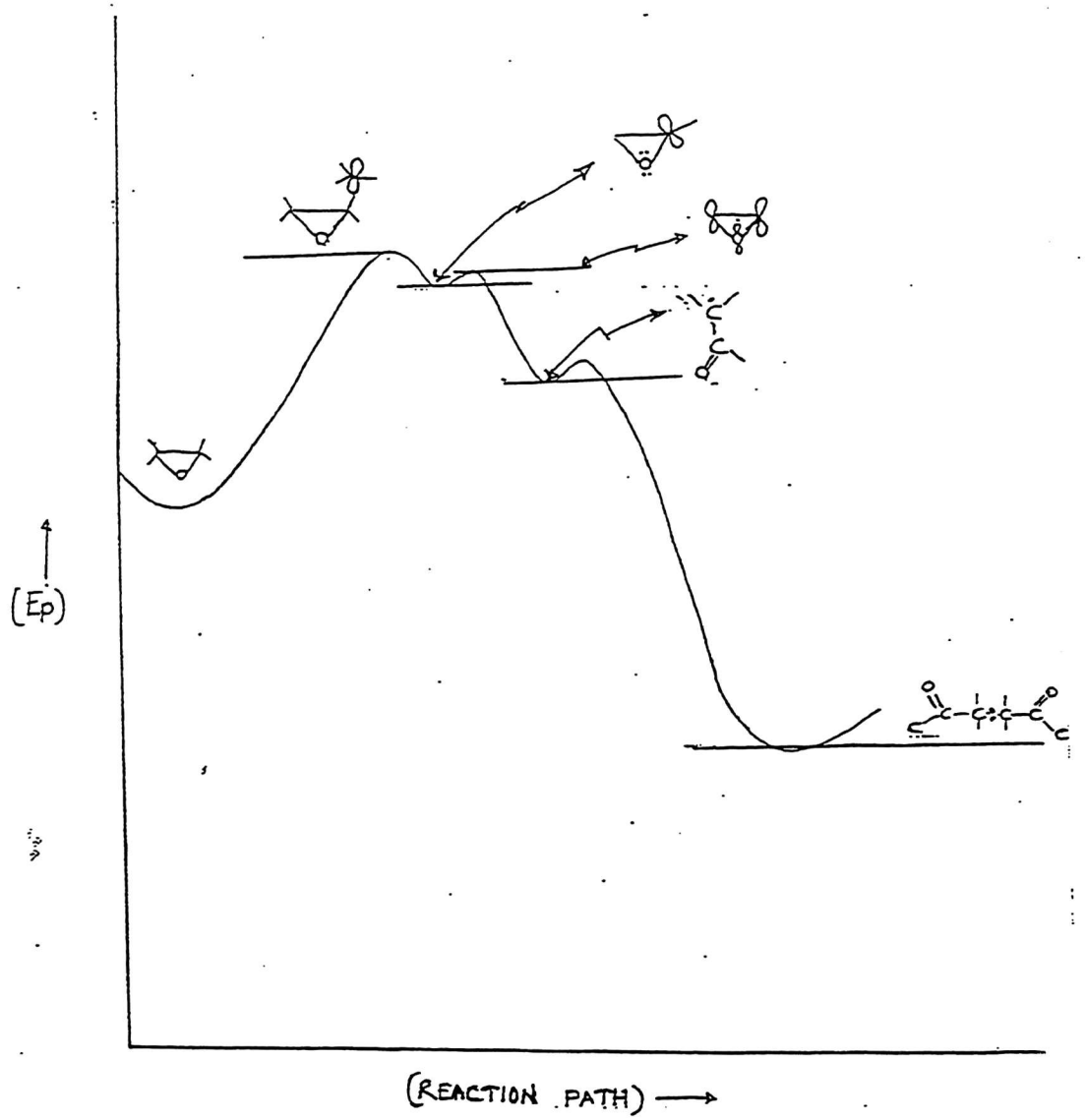


FIGURE 3

SCHEMATIC DIAGRAM OF THE PYROLYSIS EQUIPMENT

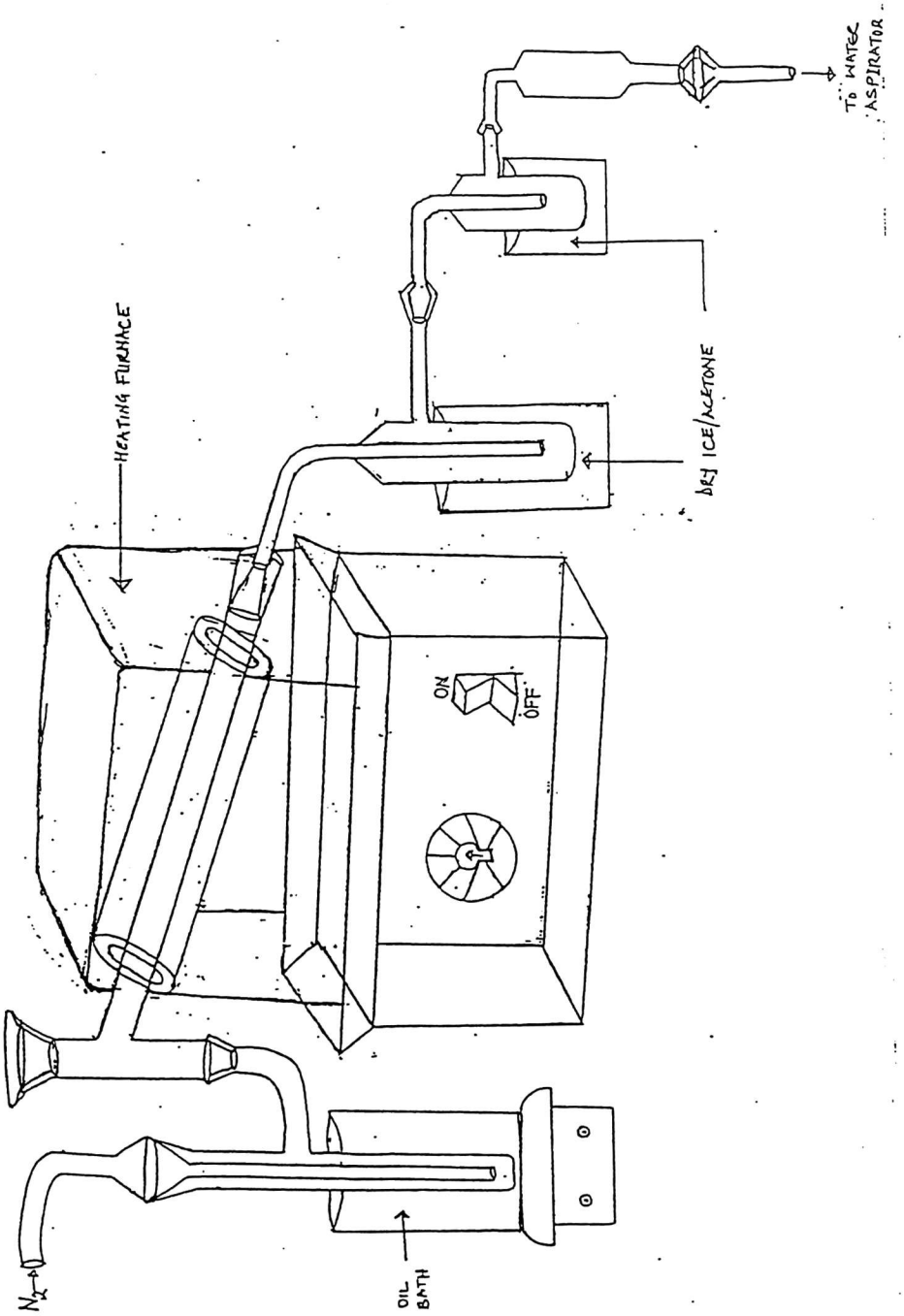


FIGURE 4

H^1 FOR PYROLYSIS OF 2,3 EPOXY BUTANE

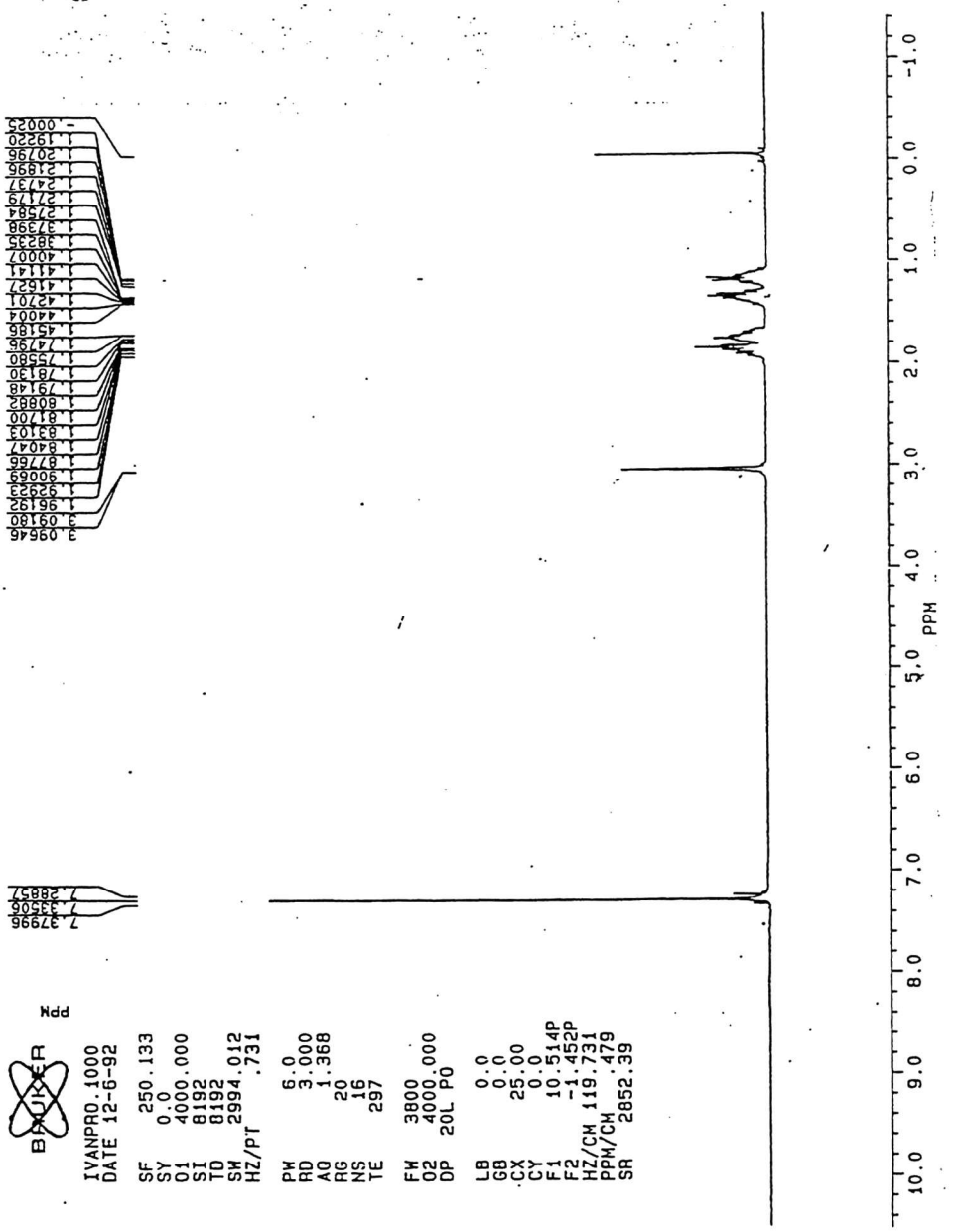


FIGURE 5

C^{13} FOR PYROLYSIS OF 2,3 EPOXY BUTANE

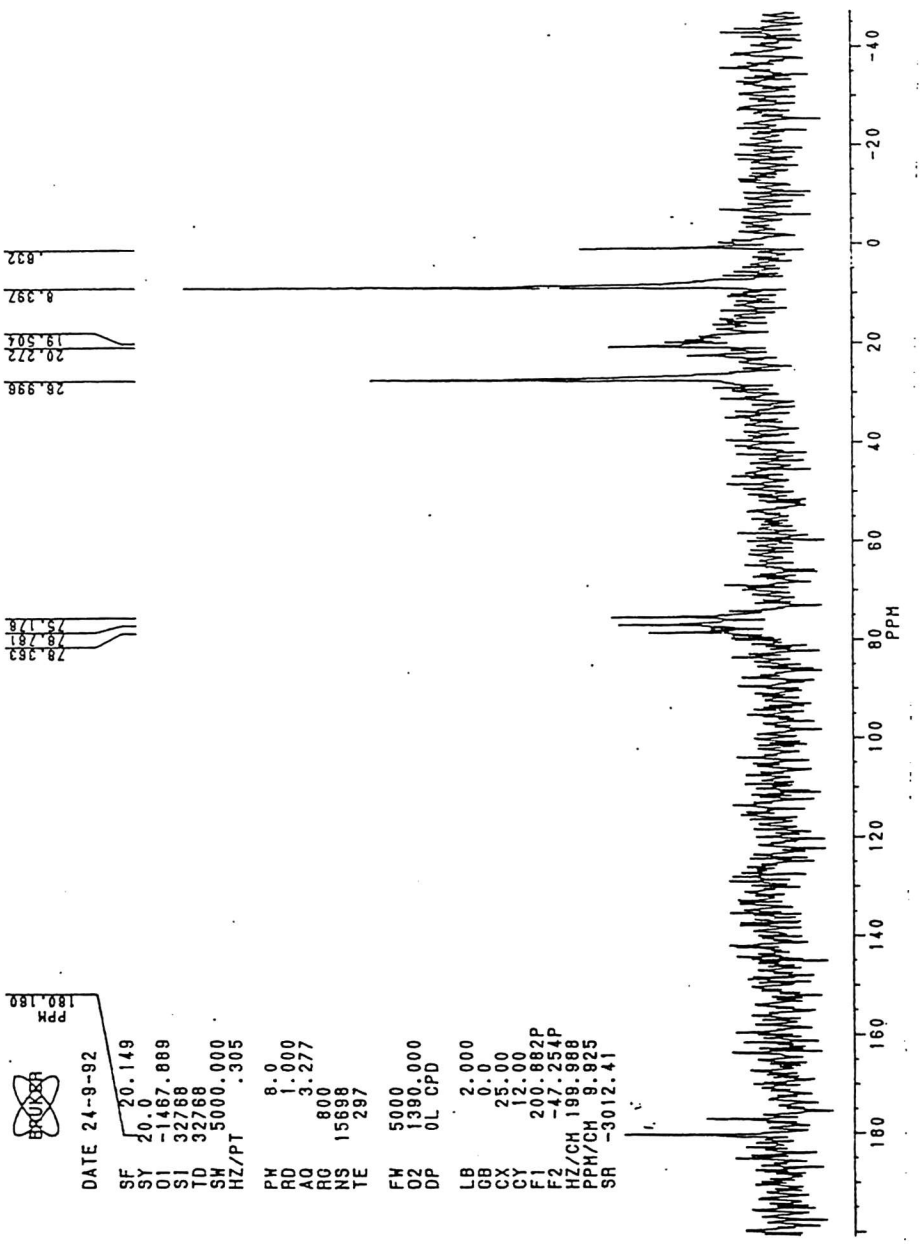


FIGURE 6

IR FOR PYROLYSIS OF 2,3 EPOXY BUTANE

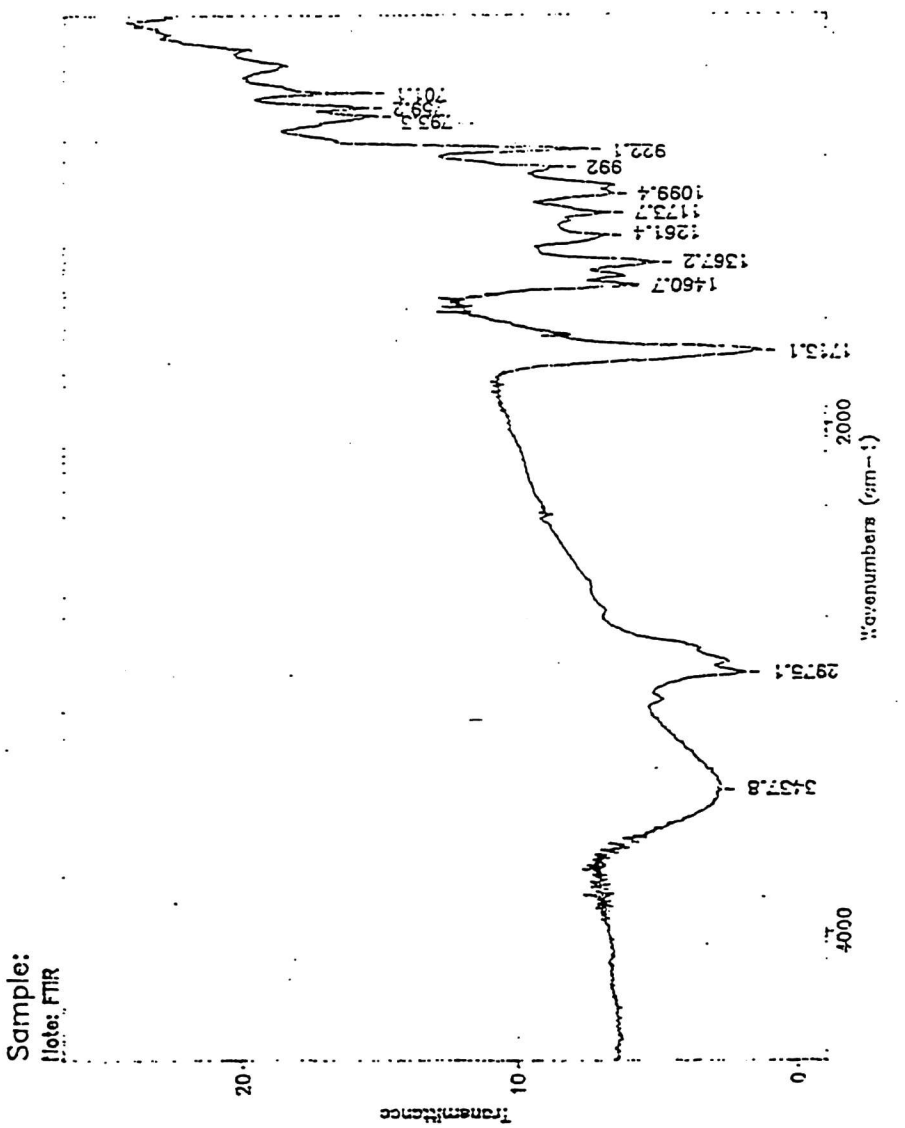
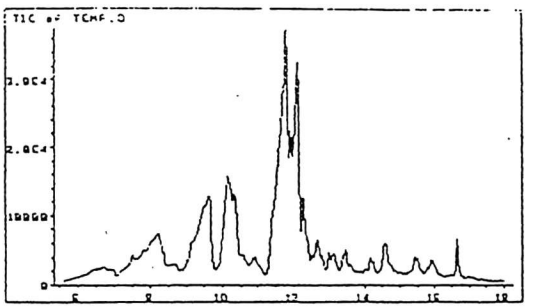


FIGURE 7

GC\MS FOR PYROLYSIS OF 2,3 EPOXY BUTANE



TABULATE
[MS1]
Scan 310 (11.596 min) of TEMP.D

Y: Scan 207 (9.598 min) of TE
X: Scan 241 (10.256 min) of T

m/z	abund.	m/z	abund.	m/z	abund.	m/z	abund.
41.0S	756	60.9S	28	77.1S	36	99.1S	308
43.0S	9129	61.9S	15	79.1S	60	100.1S	1533
44.0S	244	63.0S	15	81.1S	68	101.1S	137
45.0S	387	65.0S	38	82.1S	200	102.1S	78
50.0S	69	66.2S	24	83.1S	100	109.1S	66
51.0S	98	67.1S	353	85.1S	2842	114.2S	29
52.0S	48	68.2S	24	86.1S	181	123.2S	24
53.0S	185	69.1S	105	87.1S	78	124.1S	66
54.1S	67	70.0S	55	88.1S	39	126.1S	17
55.0S	354	71.0S	178	89.0S	32	127.1S	70
56.1S	218	72.1S	566	95.1S	18	131.1S	16
57.1S	766	73.1S	78	97.1S	18	142.2S	383
58.0S	48	74.0S	26	98.1S	13	143.1S	30
59.0S	31	75.1S	26				

TABULATE
[MS1]
Scan 335 (12.086 min) of TEMP.D

Y: Scan 241 (10.256 min) of T
X: Scan 310 (11.596 min) of T

m/z	abund.	m/z	abund.	m/z	abund.	m/z	abund.
41.0S	1072	62.0S	31	80.0S	26	100.1S	1898
43.0S	14271	63.0S	54	81.1S	203	101.1S	123
44.0S	374	64.1S	17	82.1S	324	102.1S	32
45.0S	262	65.0S	128	83.1S	130	109.1S	309
47.1S	20	66.0S	29	85.1S	3150	110.0S	28
50.0S	129	67.0S	349	86.1S	205	114.1S	37
51.0S	159	68.0S	39	87.1S	31	115.1S	20
52.0S	56	69.0S	121	88.1S	27	116.1S	17
53.0S	302	70.1S	54	89.1S	46	120.1S	75
54.0S	70	71.1S	221	91.1S	323	122.2S	22
55.0S	497	72.1S	997	92.1S	68	123.1S	74
56.1S	336	73.1S	67	93.2S	22	124.1S	201
57.1S	675	74.1S	23	95.0S	34	125.2S	27
58.1S	75	75.0S	47	96.2S	21	127.1S	96
59.0S	39	77.0S	65	98.1S	18	142.2S	456
60.0S	16	79.1S	138	99.1S	403	143.2S	44
61.1S	44						

FIGURE 8

H^1 FOR PHOTOLYSIS OF 2,3 EPOXY BUTANE BENZENE

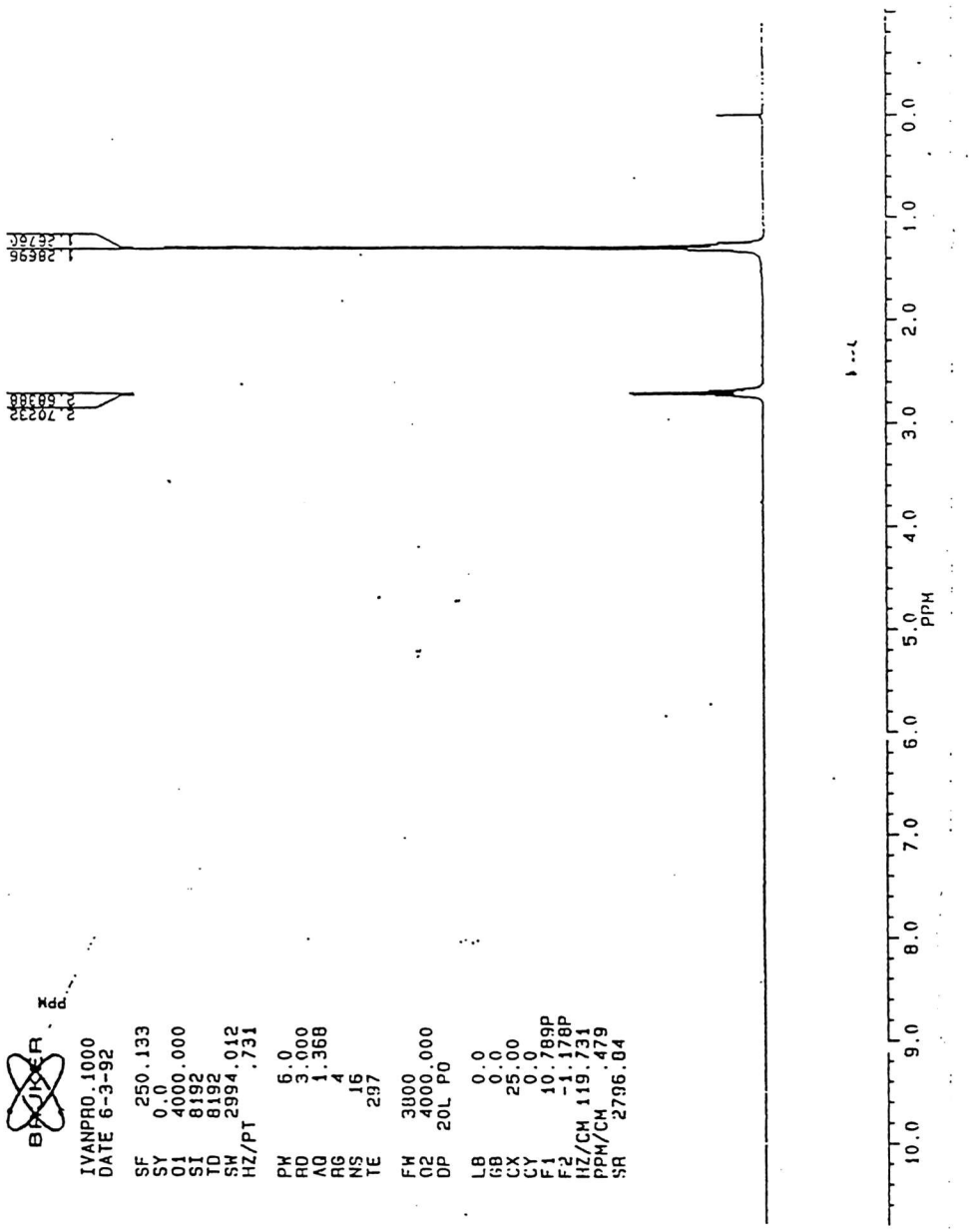


FIGURE 9

C^{13} FOR PHOTOLYSIS OF 2,3 EPOXY BUTANE BENZENE

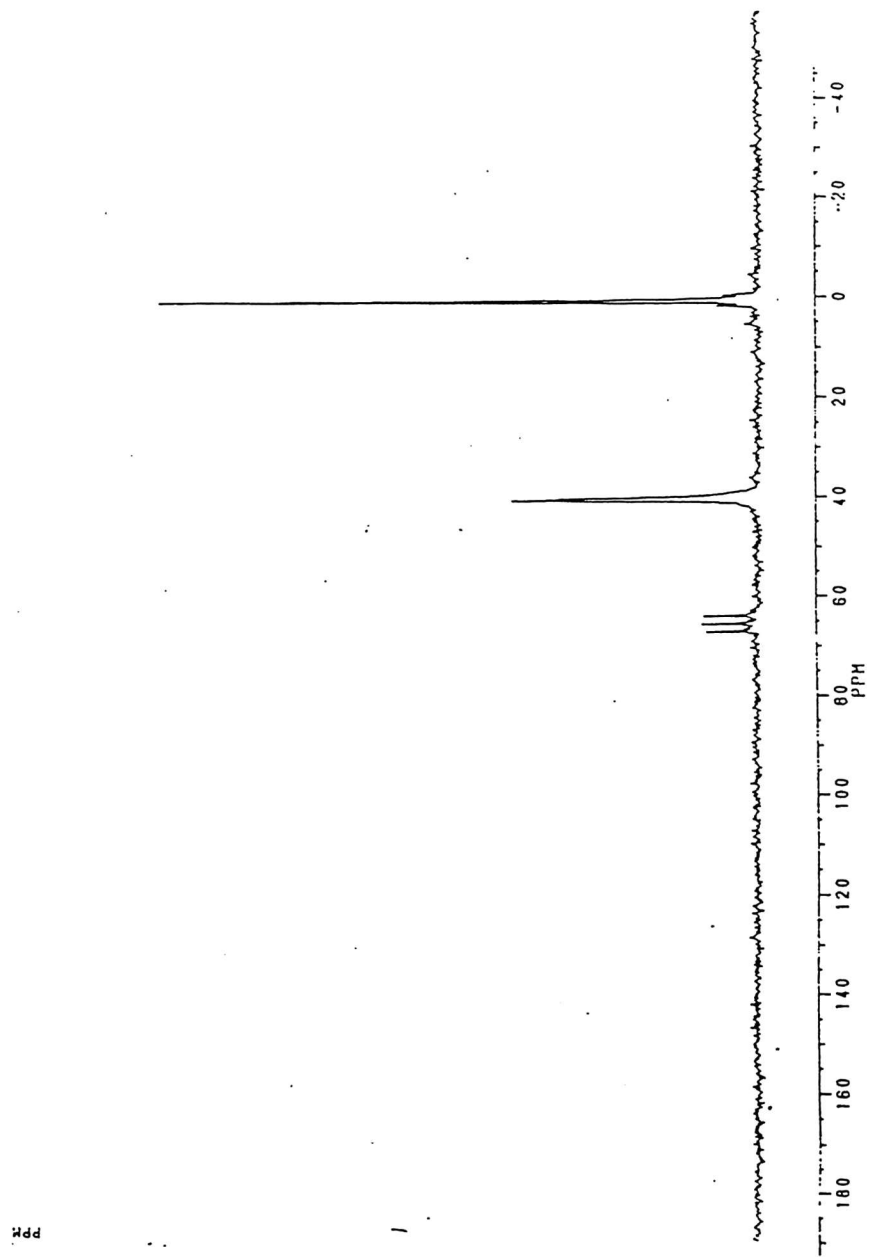


FIGURE 10

IR FOR PHOTOLYSIS OF 2,3 EPOXY BUTANE BENZENE

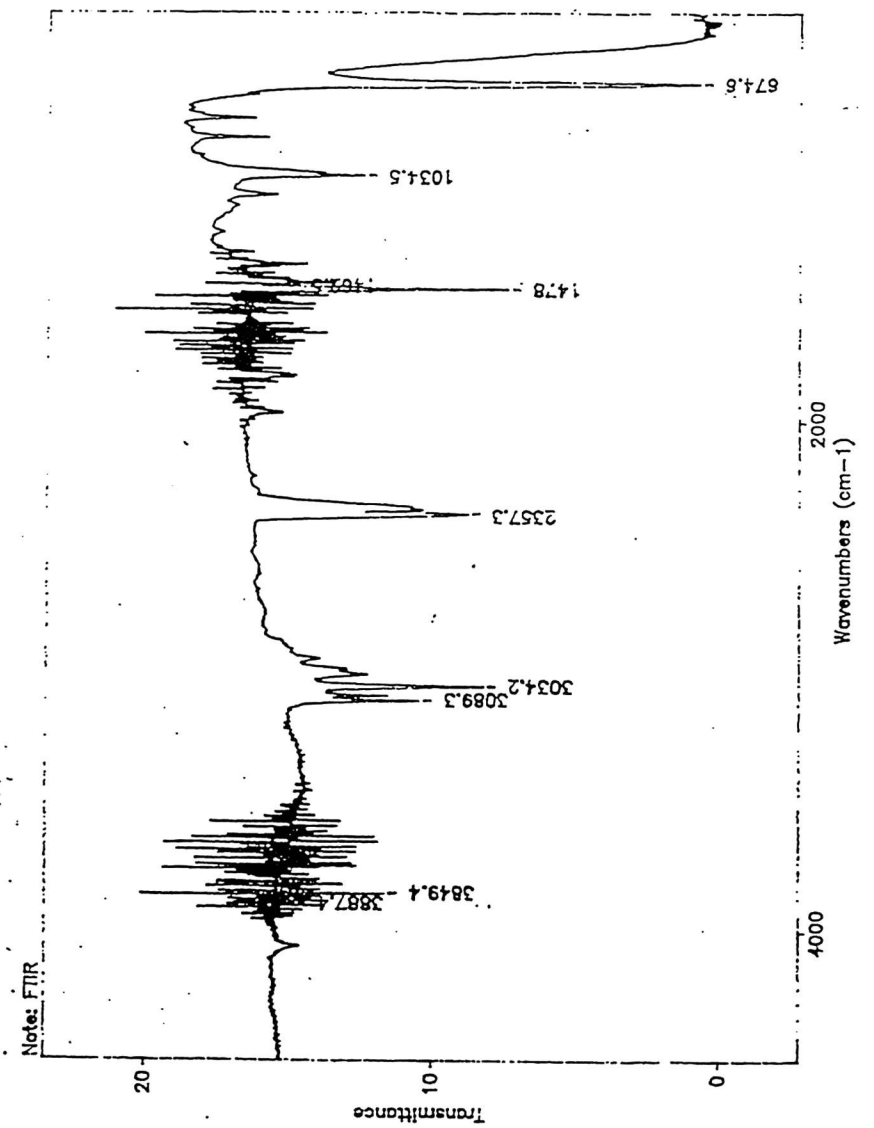
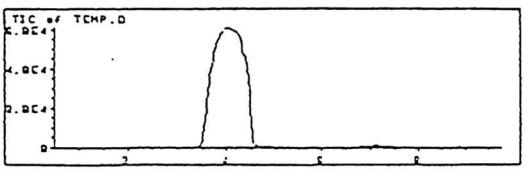
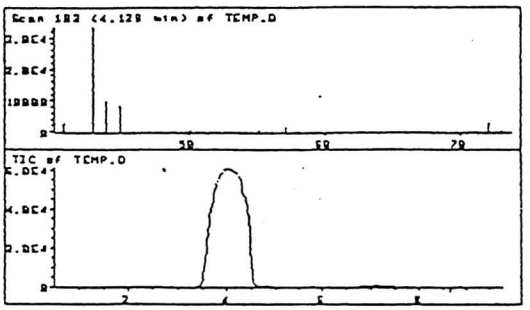


FIGURE 11

GC\MS FOR PHOTOLYSIS OF 2,3 EPOXY BUTANE BENZENE





Scan 180 (4.091 min) of TEMP.D

m/z	abund.	m/z	abund.	m/z	abund.	m/z	abund.
41.05	2606	48.15	26	54.00	78	69.00	15
43.05	32496	49.05	159	55.00	352	70.20	19
44.05	10481	50.05	471	56.10	141	71.10	186
45.05	8016	51.05	296	57.00	1244	72.10	2571
46.05	207	52.15	82	58.00	40	73.10	139
47.05	23	53.00	264				

TABULATE
[MS1]

Y: Scan 181 (4.110 min) of TE
X: Scan 180 (4.091 min) of TE

FIGURE 12

H^1 FOR PHOTOLYSIS OF 2,3 EPOXY BUTANE HEXANE

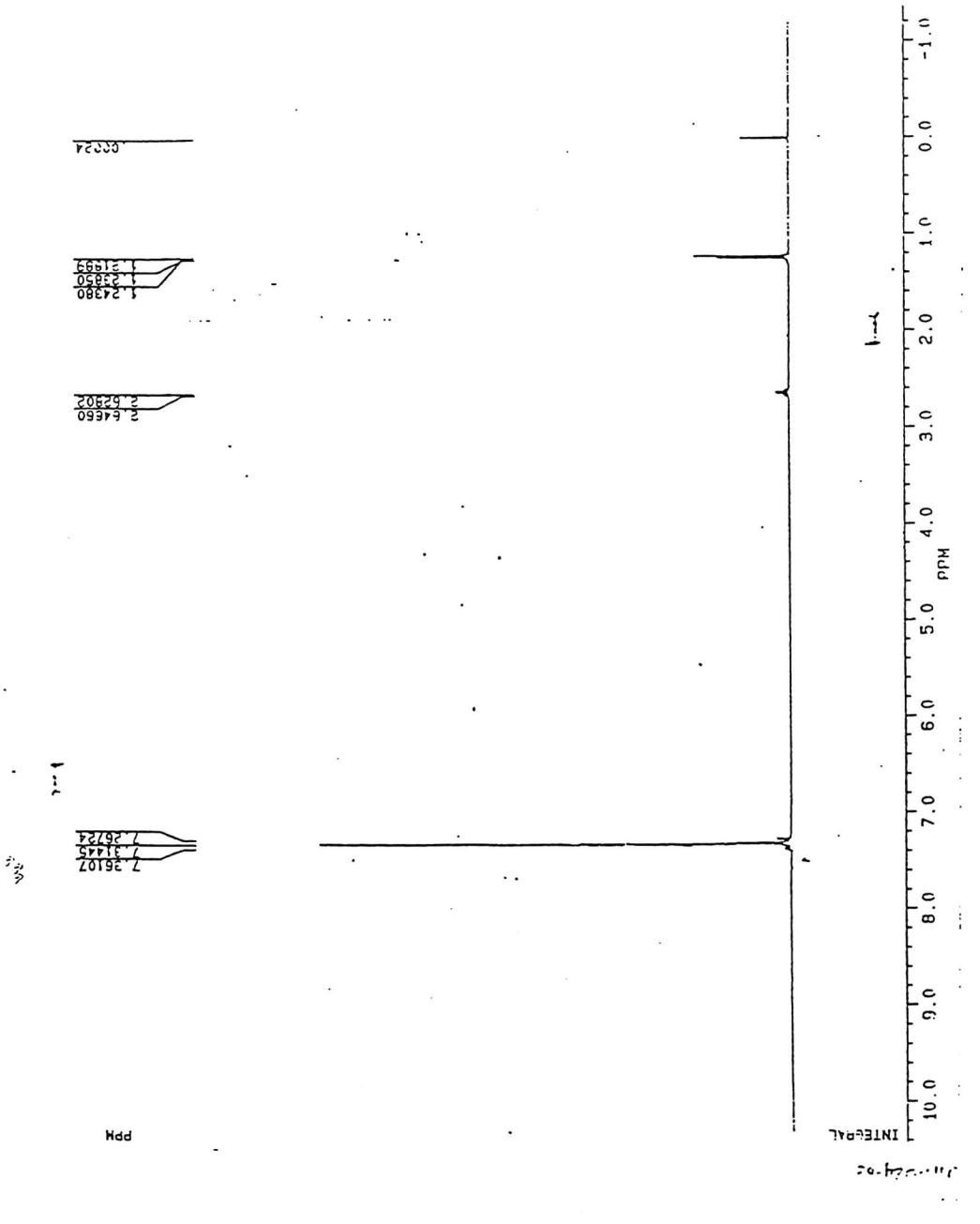


FIGURE 13

C^{13} FOR PHOTOLYSIS OF 2,3 EPOXY BUTANE HEXANE

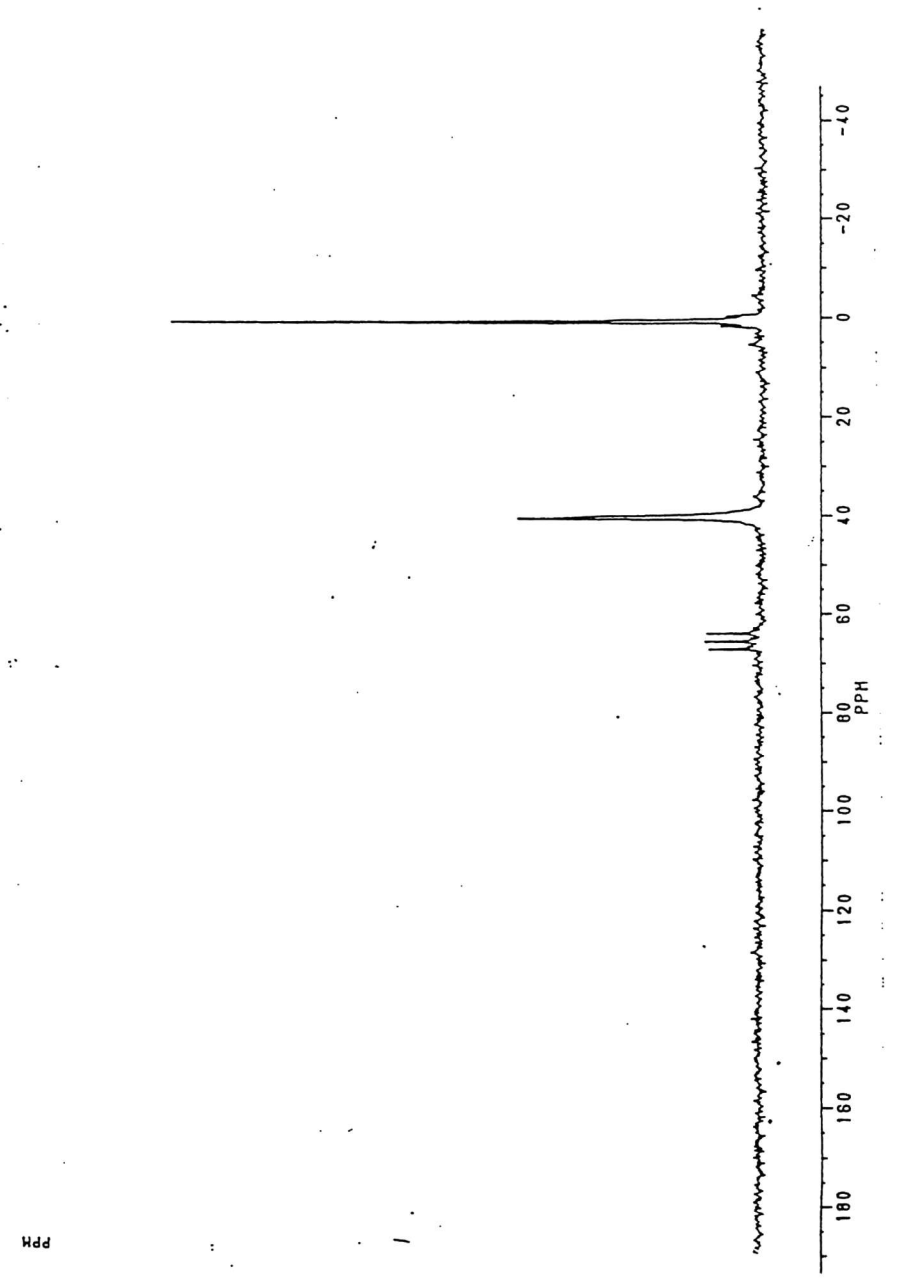


FIGURE 14

IR FOR PHOTOLYSIS OF 2,3 EPOXY BUTANE HEXANE

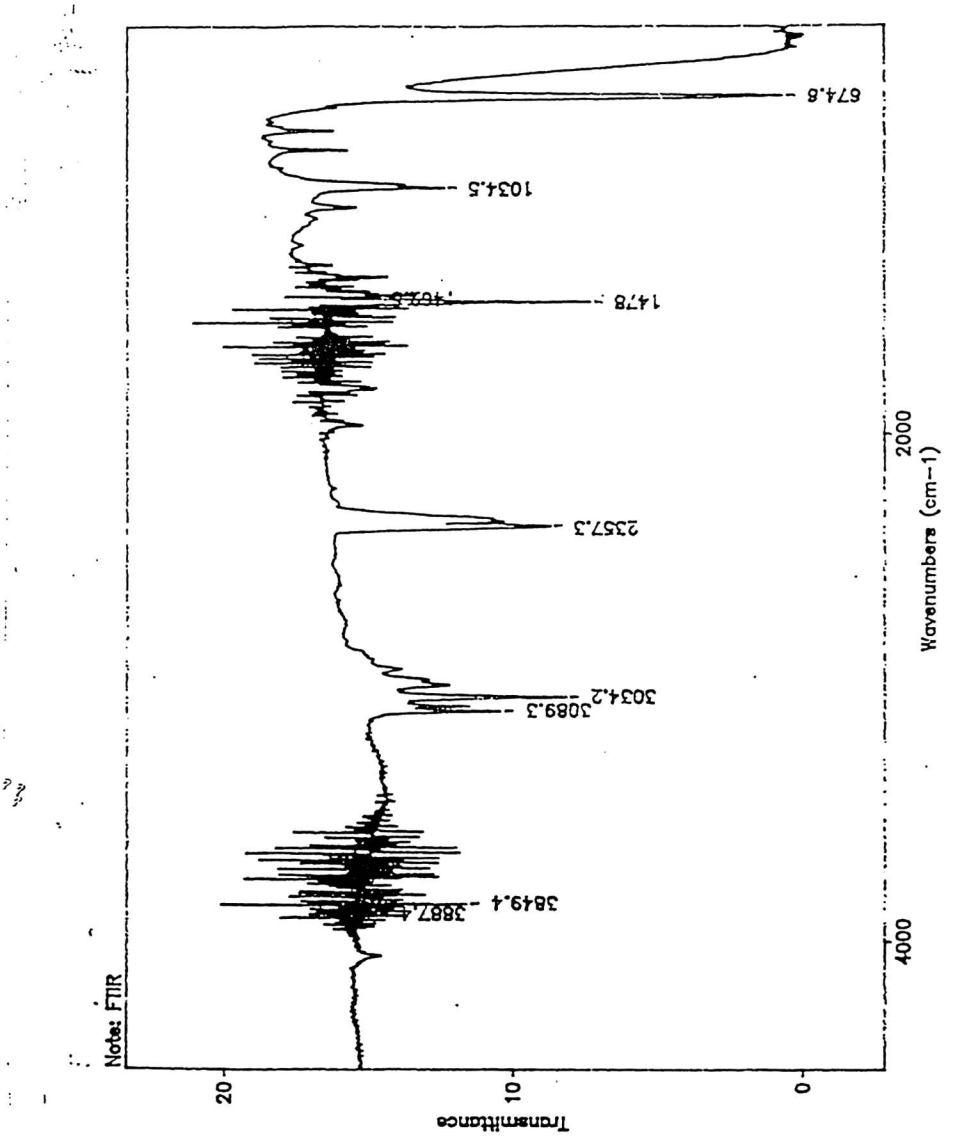
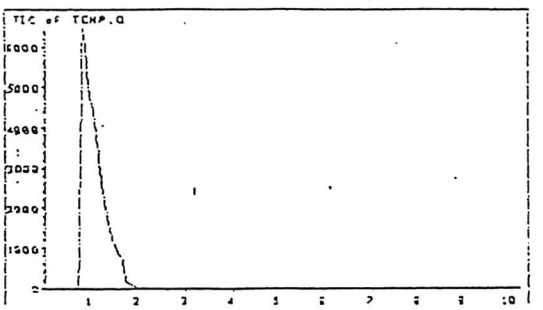


FIGURE 15

GCMS FOR PHOTOLYSIS OF 2,3 EPOXY BUTANE HEXANE



Scan 43 (1.036 min) of TEMP.D

m/z	abund.	m/z	abund.	m/z	abund.	m/z	abund.
41.05	2606	48.15	26	54.00	78	69.00	15
43.05	32496	49.05	159	55.00	352	70.20	19
44.05	10481	50.05	471	56.10	141	71.10	186
45.05	8016	51.05	296	57.00	1244	72.10	2574
46.05	207	52.15	82	58.00	40	73.10	138
47.05	23	53.00	264				

TABULATE
[MSI]

Y: Scan 181 (4.110 min) of TE
X: Scan 180 (4.091 min) of TE

FIGURE 16

H^1 FOR PYROLYSIS OF STYRENE OXIDE

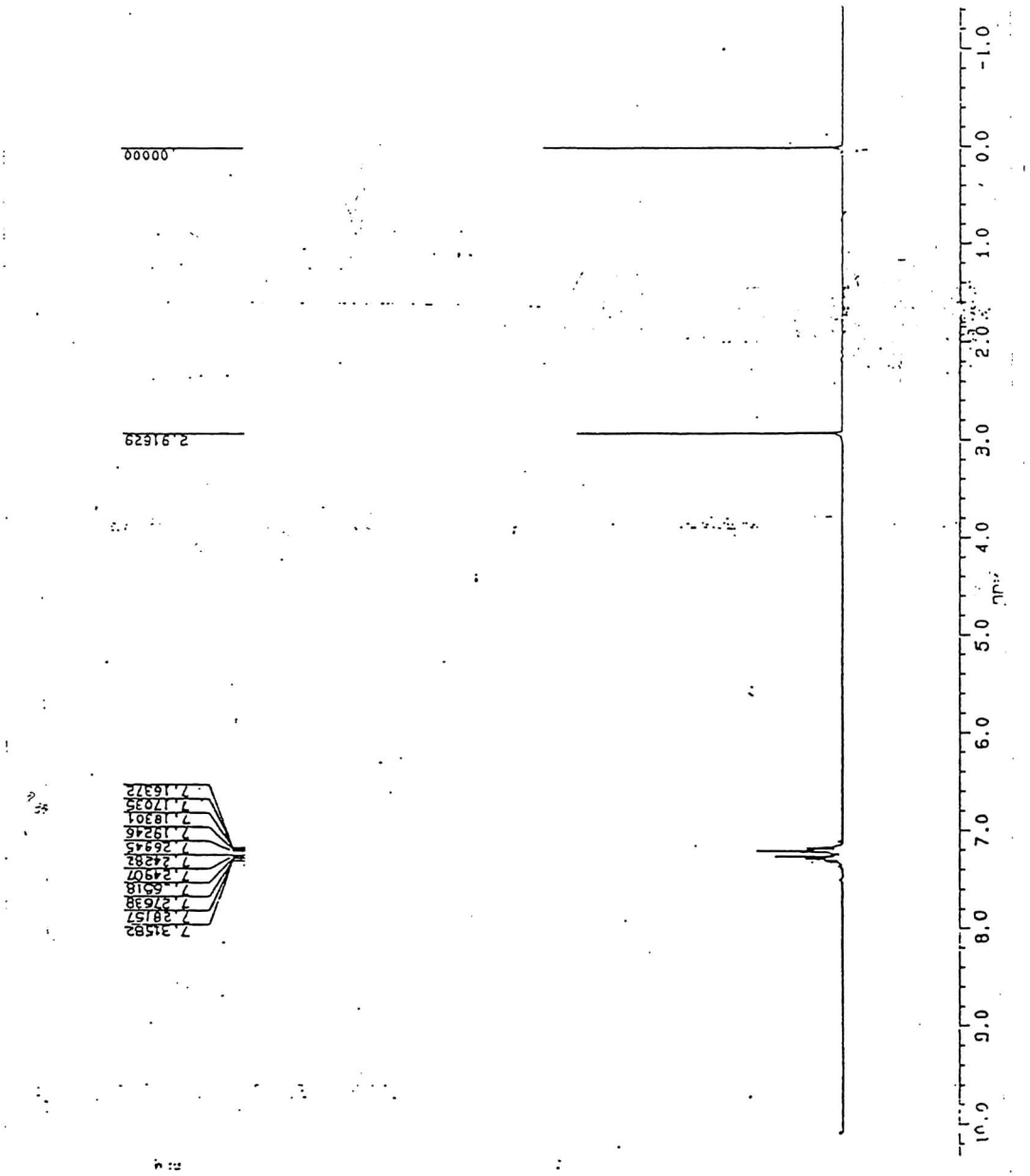


FIGURE 17

C^{13} FOR PYROLYSIS OF STYRENE OXIDE

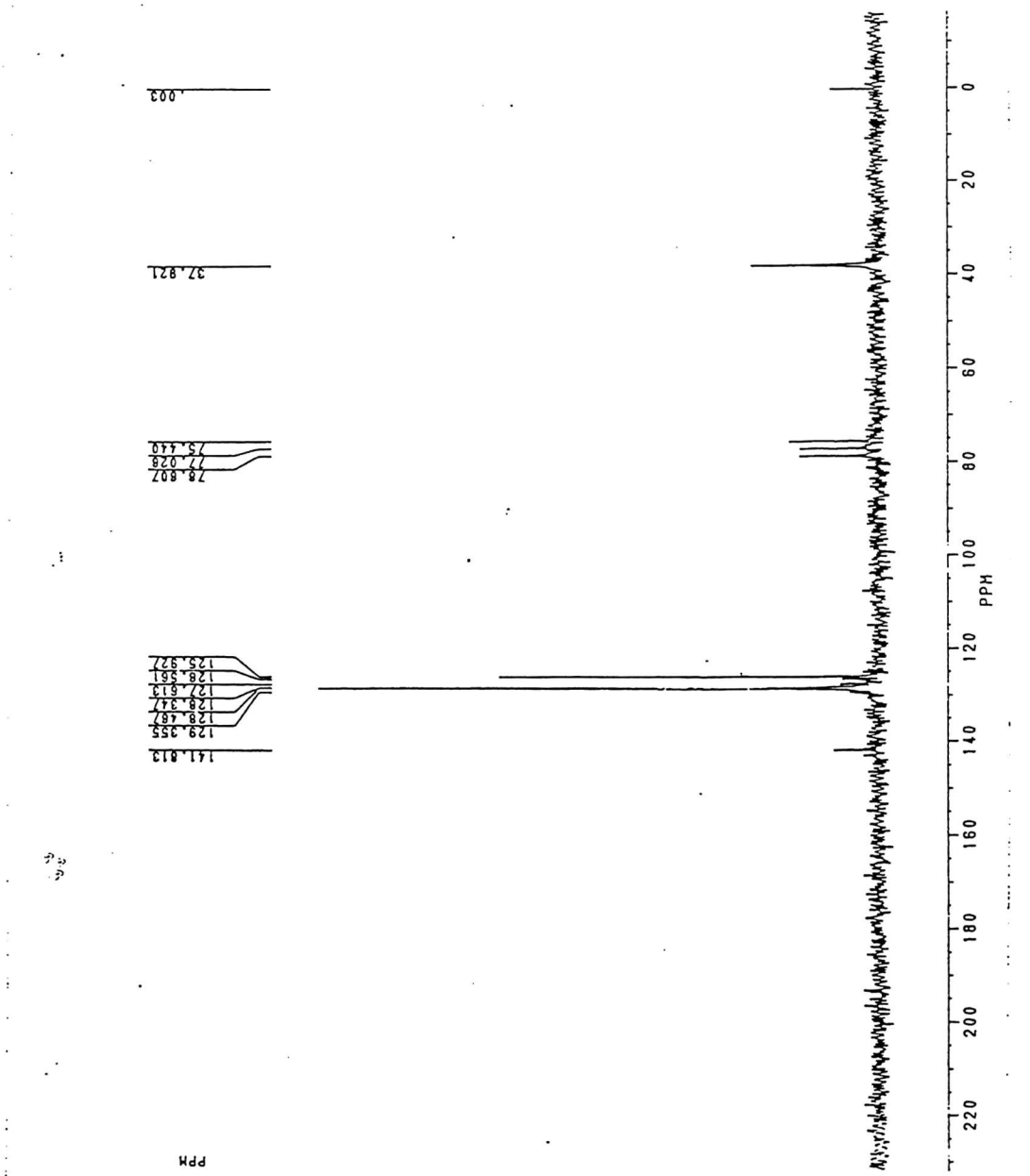


FIGURE 18

IR FOR PYROLYSIS OF STYRENE OXIDE

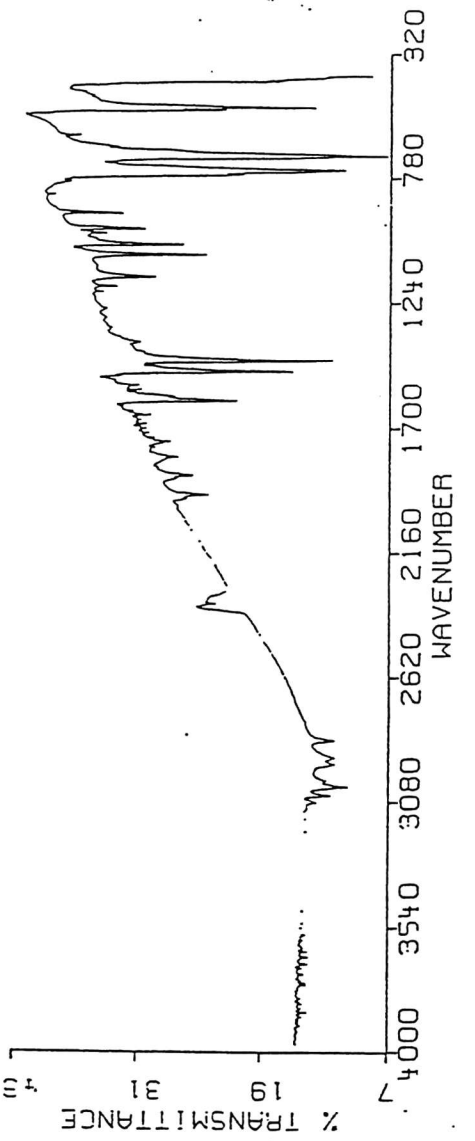
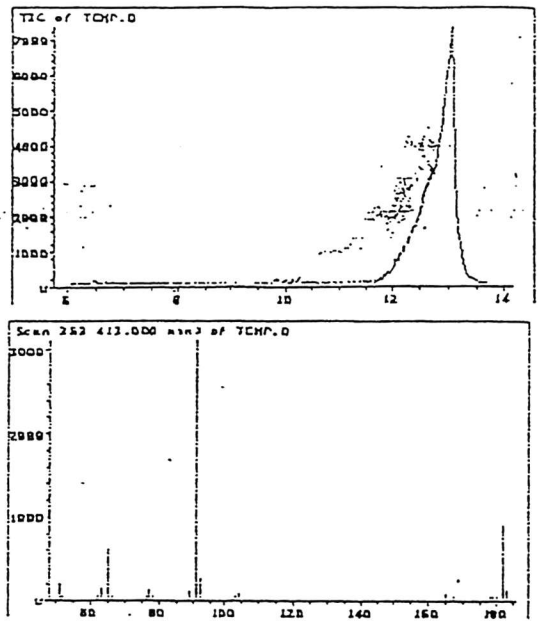


FIGURE 19

GC\MS FOR PYROLYSIS OF STYRENE OXIDE



Scan 303 (13.005 min) of TEMP.D

m/z	abund.	m/z	abund.	m/z	abund.	m/z	abund.
51.05	194	74.10	30	92.10	257	178.15	63
52.05	52	76.10	40	103.05	50	179.15	63
62.00	42	77.10	122	104.15	75	180.15	47
63.10	144	78.10	61	105.10	81	182.15	899
65.10	616	89.10	99	157.20	39	183.15	125
66.10	36	91.10	3116	168.20	35		

TABULATE
[MS1]

Y: Scan 281 (12.499 min) of T
X: Scan 303 (13.005 min) of T

FIGURE 20

H^1 FOR PHOTOLYSIS OF STYRENE OXIDE IN BENZENE

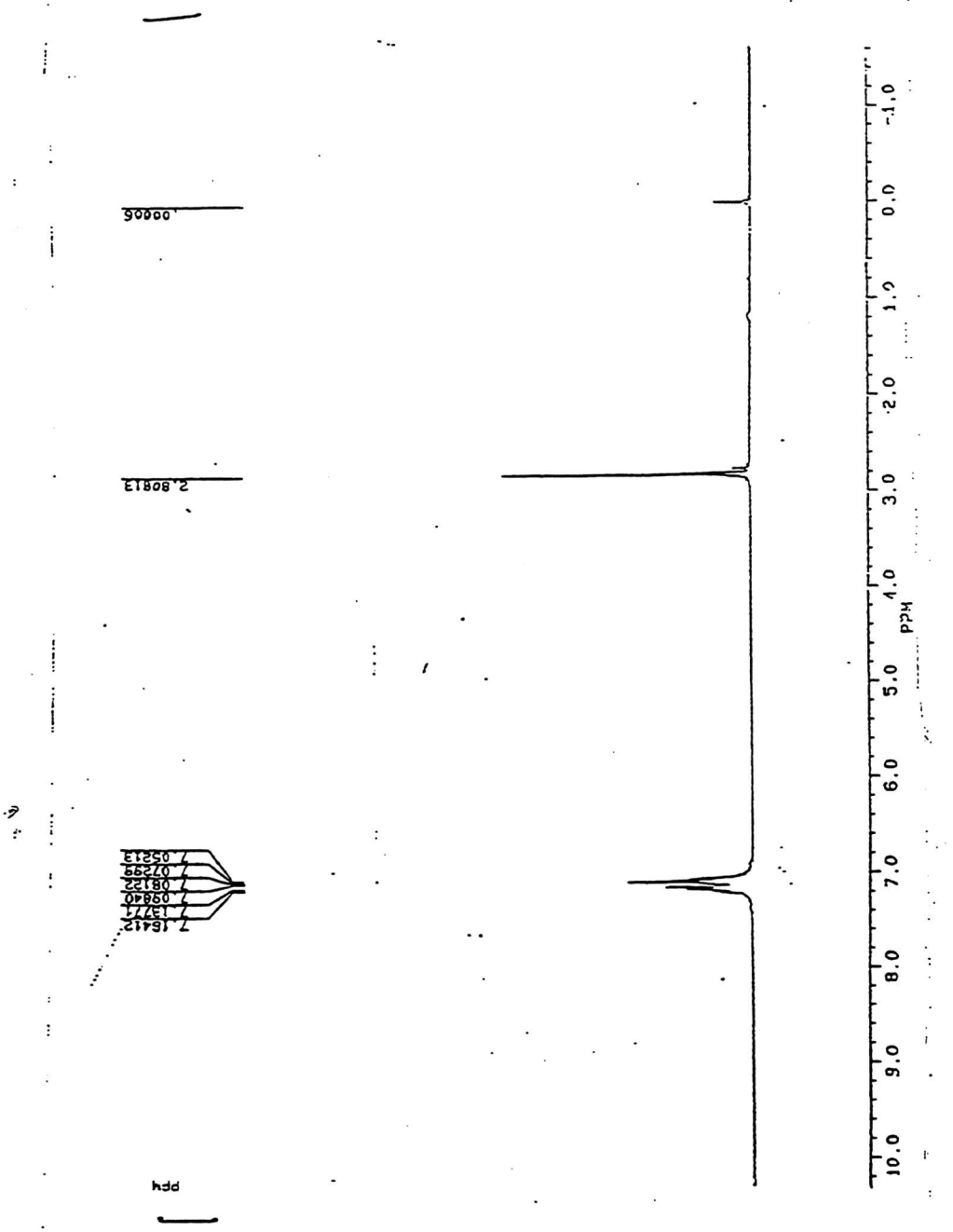


FIGURE 21

C^{13} FOR PHOTOLYSIS OF STYRENE OXIDE IN BENZENE

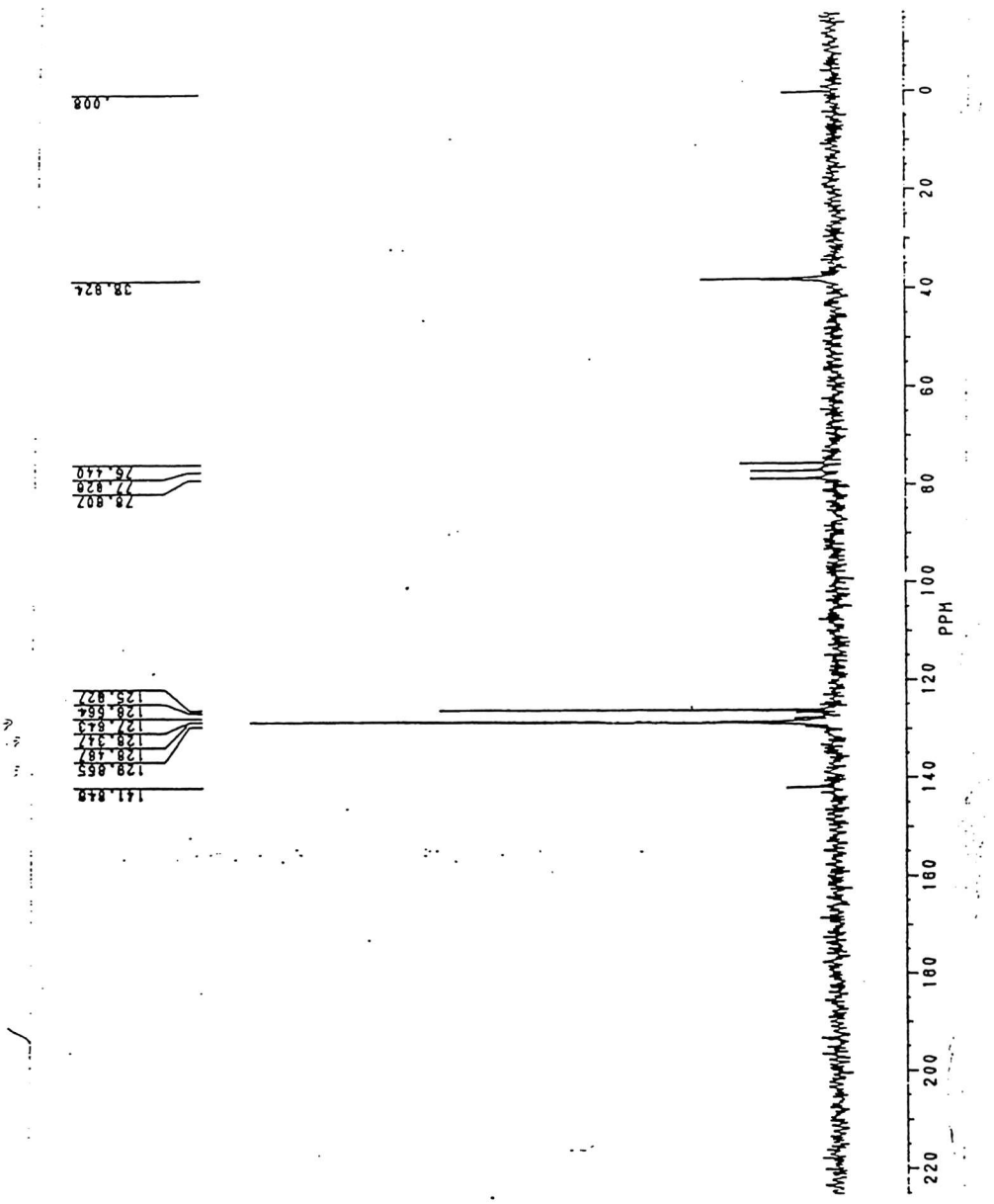


FIGURE 22

IR FOR PHOTOLYSIS OF STYRENE OXIDE IN BENZENE

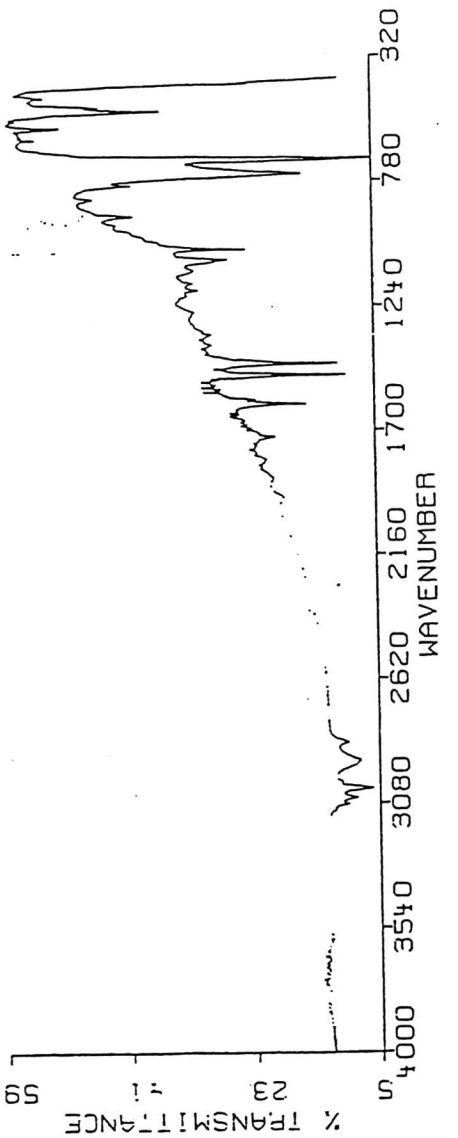
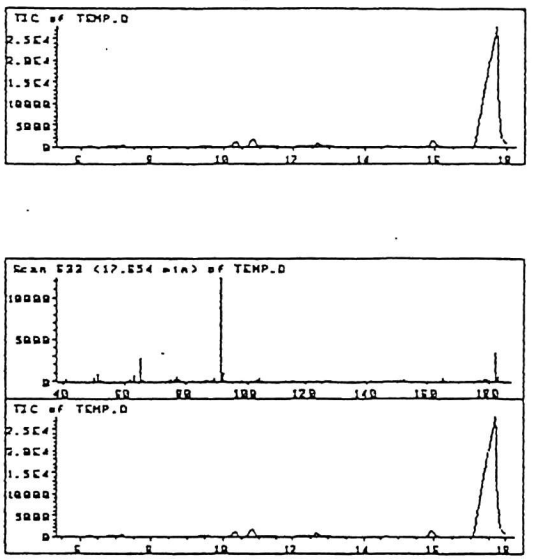


FIGURE 23

GC\MS FOR PHOTOLYSIS OF STYRENE OXIDE IN BENZENE



Scan 632 (17.654 min) of TEMP.D

m/z	abund.	m/z	abund.	m/z	abund.	m/z	abund.
41.05	260	78.10	214	104.15	316	153.10	55
50.05	340	79.10	36	105.05	39	164.15	30
51.05	849	82.10	26	113.05	17	165.05	271
52.05	200	86.10	38	115.05	95	166.05	93
53.00	52	87.10	40	116.15	19	167.15	73
61.00	25	88.15	38	126.10	31	176.15	58
62.00	143	89.05	342	127.00	36	177.15	36
63.00	604	91.05	12296	128.10	40	178.15	171
65.10	2627	92.05	907	139.10	39	179.15	108
66.10	135	93.05	31	141.10	24	180.15	45
74.00	97	98.05	20	150.20	34	182.15	3334
75.10	108	101.05	21	151.10	59	183.15	535
76.10	150	102.15	89	152.10	127	184.25	39
77.10	470	103.05	195				

TABULATE
[MS1]

Y: null.
X: Scan 632 (17.654 min) of T.

FIGURE 24

H^1 FOR PHOTOLYSIS OF STYRENE OXIDE IN HEXANE

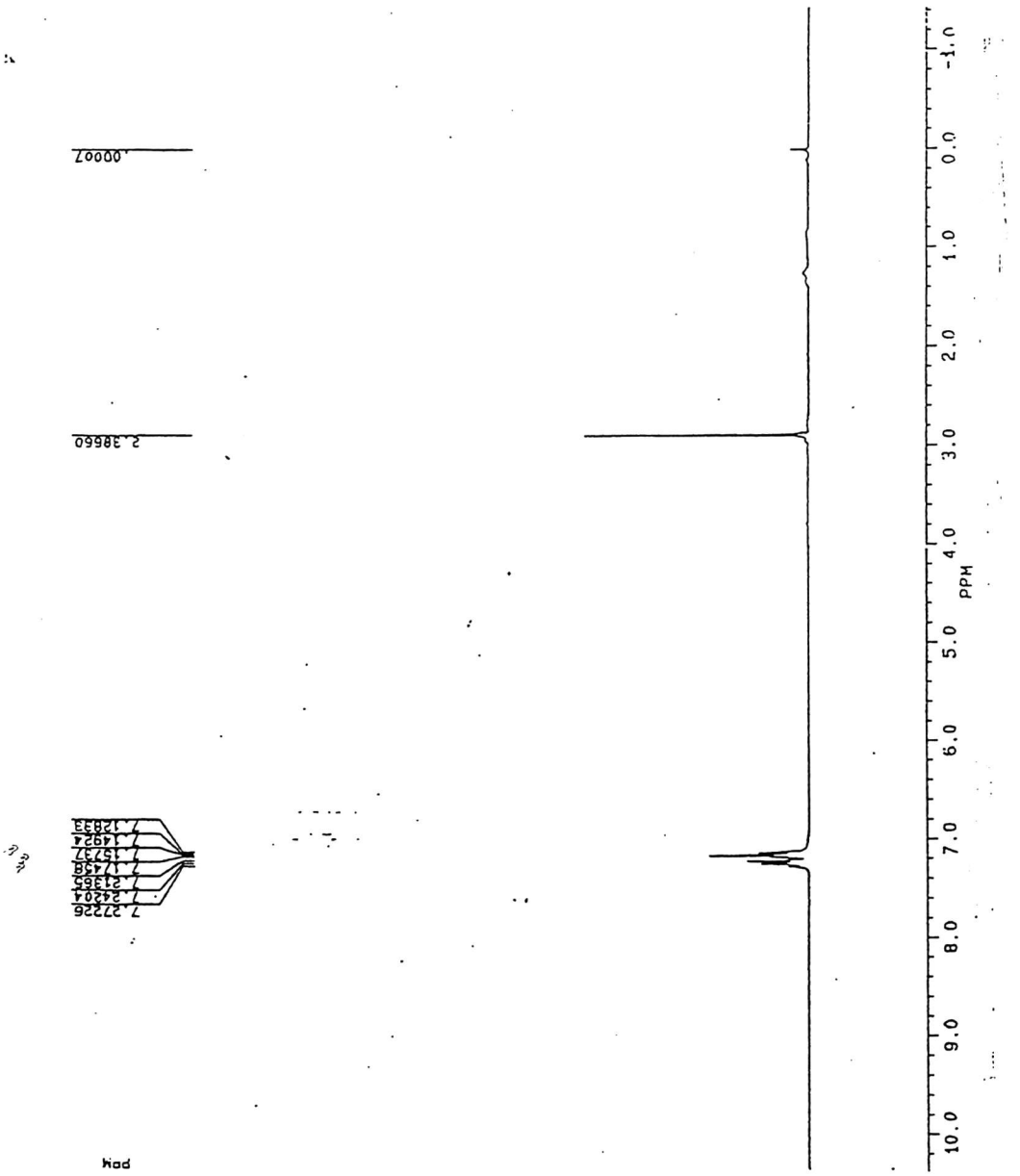


FIGURE 25

C^{13} FOR PHOTOLYSIS OF STYRENE OXIDE IN HEXANE

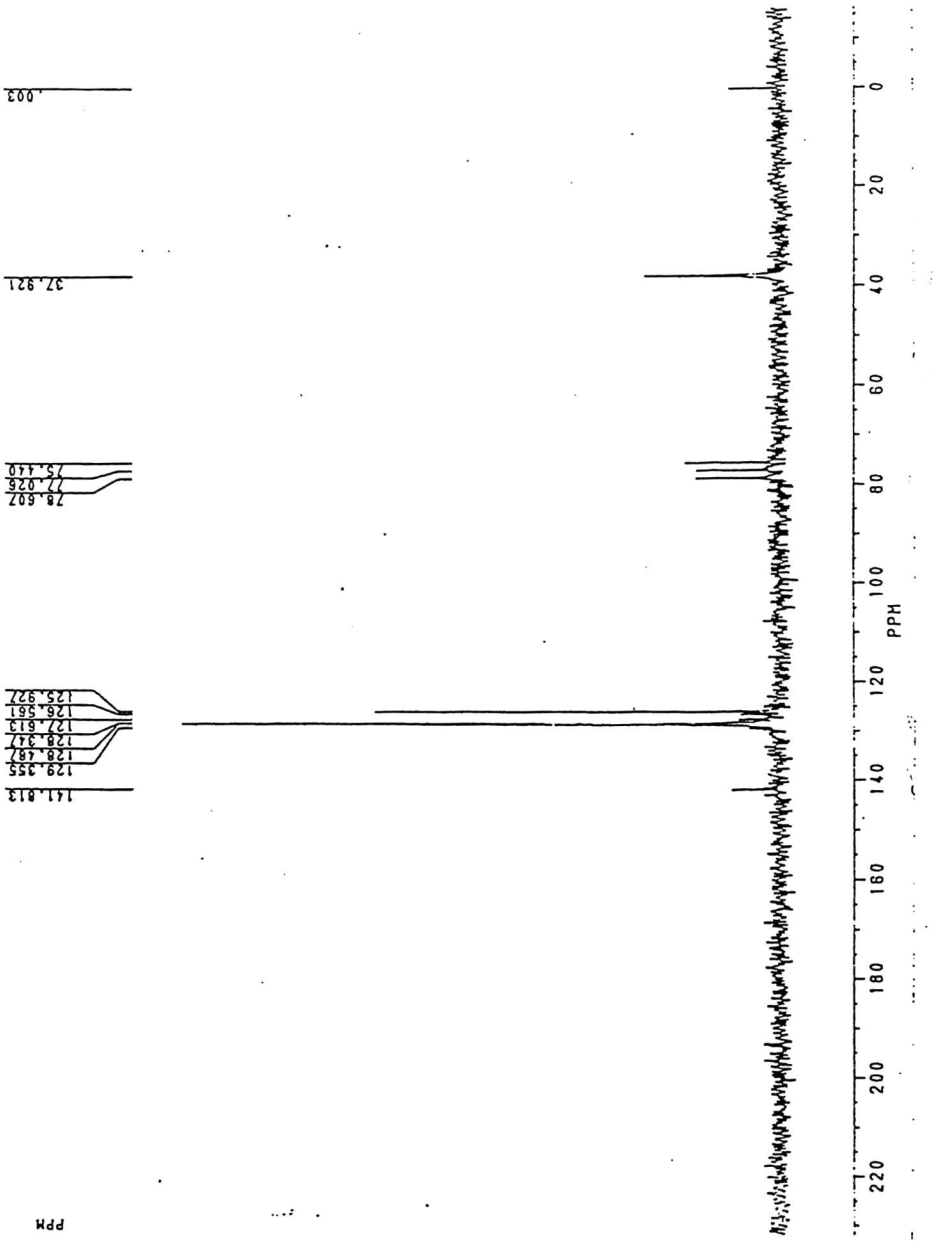


FIGURE 26

IR[1] FOR PHOTOLYSIS OF STYRENE OXIDE IN HEXANE

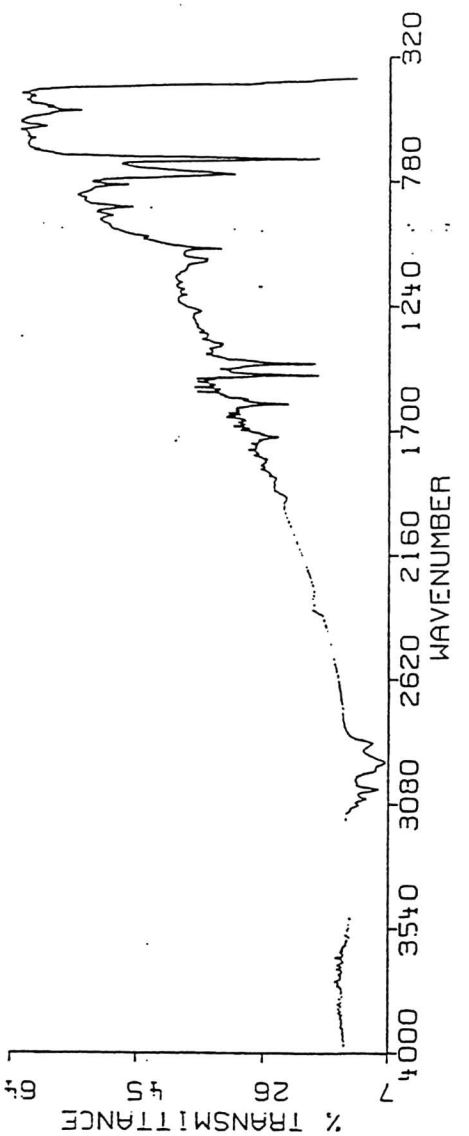
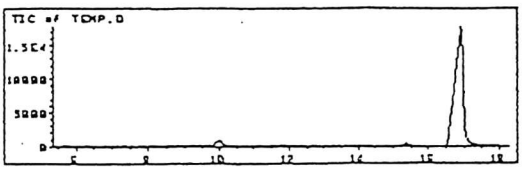
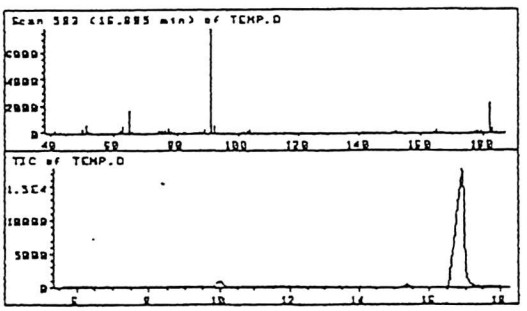


FIGURE 27

GC\MS FOR PHOTOLYSIS OF STYRENE OXIDE IN HEXANE





Scan 593 (16.895 min) of TEMP.D

m/z	abund.	m/z	abund.	m/z	abund.	m/z	abund.
41.05	159	77.10	328	101.05	16	153.20	26
42.95	24	78.10	127	102.05	62	164.15	16
50.05	223	79.00	29	103.05	116	165.15	173
51.05	554	82.10	16	104.05	211	166.15	61
52.05	140	82.60	13	105.05	25	167.15	38
53.00	43	86.00	22	115.05	63	176.15	35
62.00	92	87.10	33	126.00	23	177.15	25
63.00	392	88.25	29	127.10	21	178.15	117
65.10	1631	89.05	230	128.10	32	179.15	68
66.00	87	91.05	7781	139.10	24	180.15	23
74.10	71	92.05	557	141.20	14	182.15	2203
75.10	69	93.15	27	151.10	38	183.15	347
76.10	103	97.95	15	152.10	84	184.25	27

TABULATE
[MS1]

Y: null.
X: Scan 593 (16.895 min) of T

FIGURE 28

H^1 FOR PHOTOBROMINATION OF STYRENE OXIDE

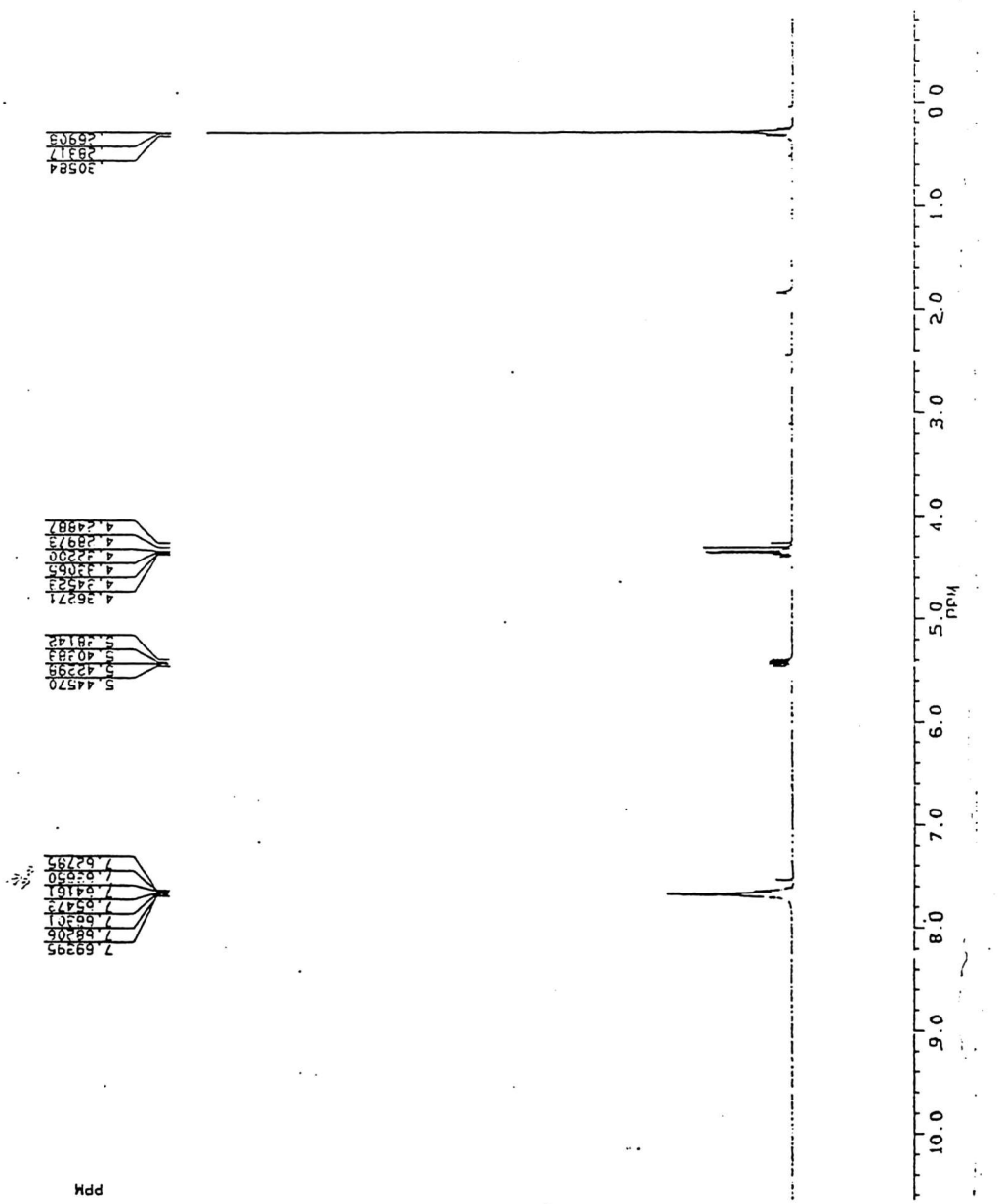
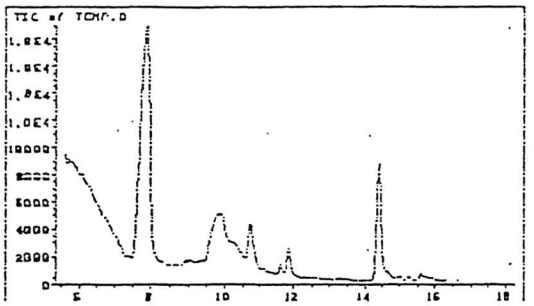
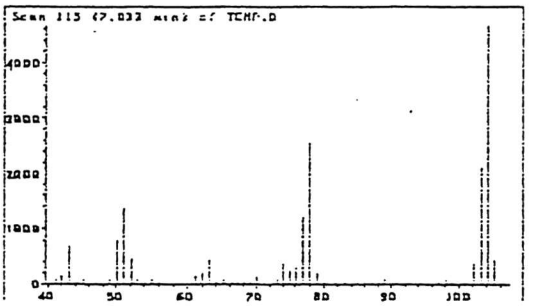


FIGURE 29

GC\MS FOR PHOTOBROMINATION OF STYRENE OXIDE





Scan 115 (7.833 min) of TEMP.D

m/z	abund.	m/z	abund.	m/z	abund.	m/z	abund.
41.15	84	55.00	14	73.00	97	88.10	39
42.05	139	57.00	40	74.10	351	89.05	90
43.05	552	60.00	24	75.10	237	97.05	25
44.15	39	61.10	141	78.10	273	98.05	84
45.15	85	62.00	184	77.10	1185	99.05	18
49.05	88	63.00	408	78.10	2516	101.05	44
50.05	813	64.00	45	79.10	182	102.15	363
51.05	1342	65.10	75	80.10	28	103.15	2065
52.15	439	67.20	13	83.10	26	104.15	4652
53.05	81	68.10	26	85.00	16	105.15	417
54.10	37	69.10	45	86.00	19	106.05	31
55.00	88	70.10	107	87.10	35		

TABULATE
[MS1]

Y: null.
X: Scan 115 (7.833 min) of TE

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